EFFECT OF ENVIRONMENT ON THE FATIGUE AND THE TENSILE PROPERTIES OF GLASS FIBER REINFORCED VINYL ESTER AND EPOXY THERMOSETS

BY

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This thesis, written by Mohammed Shafeeq under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN MECHANICAL ENGINEERING.**

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عمادة الدراسات العليا
DEANSHIP OF GRADUATE STUDIES

Dedicated

to

my beloved Parents, Sister & Brother-in-law

whose constant prayers, sacrifice and inspiration led

to this accomplishment.

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All praise be to Allah (s.w.t) for his limitless blessing and guidance. May Allah bestow peace on his Prophet Mohammed (peace and blessings of Allah be upon him), and his family. Acknowledgements are due to King Fahd University of Petroleum and Minerals for the support in carrying out this research.

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THESIS ABSTRACT

Name: MOHAMMED SHAFEEQ

Title: EFFECT OF ENVIRONMENT ON THE FATIGUE AND THE TENSILE PROPERTIES OF GLASS FIBER REINFORCED COMPOSITES

Major Field: MECHANICAL ENGINEERING

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During the long-term exposure of Fiber Reinforced Plastic (FRP) pipes, material degradation is expected to occur in the matrix, fiber, and the fiber-matrix interfacial regions. The degradation rate may be constant or increase/decrease with time and can be gradual and abrupt. These changes in the degradation mechanisms may also occur during the long-term exposure. All of these issues raise serious concerns regarding the long-term durability of the FRP pipes and constitute problems that require solutions before extensive use of the FRP pipes is made to replace their metallic counterparts.
The objective of this research is to investigate the effect of environment on the performance of vinyl ester and epoxy based glass fiber-reinforced thermoset composite pipes intended for use in oil and seawater transportation. In these applications, the pipes are subjected to both static (design stress) and cyclic loads (pressure fluctuation). The effects of wide range of accelerated and the natural environments on the tensile and the fatigue behavior were explored. The accelerated conditions include Dry heat, UV radiation, humidity, seawater & salt water immersion, salt fog, and oxygen saturated salt water. The fractographic analysis of the specimens were done to evaluate environmental effect on the fracture process in the pipes.

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ملخص الرسالة

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عنوان الرسالة: تأثير البيئة على خصائص الشد والإعياء على المركبات المقواة بالألياف الزجاجية

التخصص: الهندسة الميكانيكية

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خلال تعرض الانابيب البلاستيكية المقواة بالألياف الزجاجية لعوامل البيئة المختلفة يتوقع حدوث تآكل في النسيج والألياف ومناطق نسج الألياف في مادة تلك الأنابيب. معدل التآكل قد يكون ثابتا او متزايدا او متناقصا مع الزمن وقد يكون تدريجي او مفاجئ. وهذه التغيرات في ميكانيكية التآكل تحدث في الغالب عند التعرض لمدة طويلة من الظروف البيئية.

كل هذه القضايا والمشاكل تظهر بجدية عند تعرض الانابيب المقواة بالالياف الزجاجية لظروف بيئية لمدة زمنية طويلة وهي بحاجة الى وضع حلول لها قبل التركيز على استعمال هذه الانابيب وطرح استخدامها بدل الانابيب المعدنية.

الهدف من هذا البحث هو فحص تأثير البيئة على أداء الانابيب المقواة باللألياف الزجاجية والمبنية على مادتي فاينل استر وايبوكسي وذلك عندما تستعمل هذه الأنابيب في نقل النفط والزيوت ومياه البحار. في هذه التطبيقات تم تعريض هذه الانابيب لقوة ضغط ساكنة (قوة شد التصميم) وقوى ضغط متغيرة, وتم دراسة وبحث تأثير مدى كبير من الظروف البيئية المتسارعة والطبيعية على خصائص الشد والإعياء في هذه الأنابيب. الظروف المتسارعة اشتملت على : الحرارة الجافة, الرطوبة, الغمر في مياه مالحة ومياه البحر, الضباب الملحي, مياه بحار مشبعة بالأوكسجين و إشعاع (UV) . تم عمل تحليل فراكتوغرافيك للعينات لتقييم تأثير الظروف البيئية في أثناء تشقق تلك الانابيب.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

Chapter 1

Introduction

1.1 General Background

The present day increasingly complex design for engineering components and structures, the demand for superior performance, and the weight saving requirements propelled the material scientists, engineers and designers into a continued search for new materials. Since 1960's, when the first fiber reinforced plastics were developed, the extent and scope of their application has been continuously expanding.

A composite is a heterogeneous combination of two or more materials (reinforcing agents & matrix), differing either in form or composition on a

macro-scale. The combination results in a material that maximizes specific performance properties. The constituents do not dissolve or merge completely and therefore normally exhibit an interface between one another. In this form, both reinforcing agents and matrix retain their physical and chemical identities, yet they produce a combination of properties that cannot be achieved with either of the constituents acting alone. A laminate structure consists of two or more relatively thin, stiff, and strong faces joined by relatively thick layer of adhesive. A composite structure tends to be stiffer and stronger than a solid laminate. Based on the type of matrix used, the composites can be classified as polymer matrix, metal matrix and ceramic matrix composites. In fiber-reinforced composites, fibers are the principal load carrying members, while the surrounding matrix keeps them in the desired location and orientation. Matrix also acts as a load transfer medium between the fibers, and protects them from environmental damages due to elevated temperatures, humidity and corrosion. The principal fibers which are currently in commercial use are various types of glass, aramid, boron, carbon and Kevlar. All these fibers are incorporated into a matrix either in continuous or discontinuous form.

Polymer matrix composites (PMCs) have come into existence due to the

need for high specific strength materials. Thirty years ago, this need for high strength to weight materials was in the aerospace industry, where every ounce saved improves performance. Thus, the aerospace industry spent time and money creating high performance composite materials. With the success in aerospace, composite technology began to be a viable material solution in other applications, such as automobile, marine, sports, and civil infrastructure and aqueous and gaseous medium transport pipelines. Unlike the aerospace industry, cost played an important role. Polymeric composites offer many advantages over its counterparts such as metals. Considerable amount of research has been undertaken on the issue of durability of composites in civil infrastructure and marine applications [1]. However research in relevance to the polymer composite pipelines, still lags much behind the expanding applications. Polymer composite properties vary depending on the manufacturing methods. The properties of the final composite will depend on the following.

1. Class of polymer resin and type of reinforcing agents
2. Chemical additives and modifiers
3. Method of manufacturing

4. Percentage and orientation of the fiber reinforcement.

Composites have unique properties as follows:

1. Composite materials are 30-45% lighter than aluminum structures designed for the same functional requirements

2. Pipes/cylinders made of composites, with lower weight compared to the metallic ones, can withstand high internal pressures

3. Excellent corrosion resistance

4. Appropriate inhibitors/additives can impart very good fire retardant properties in composites

5. Improved torsional stiffness and impact resistance properties

6. High fatigue endurance limit (up to 60% of the ultimate tensile strength)

7. Excellent resistance to Creep, Creep rupture and wear.

8. Design flexibility (composites are more versatile than metals and can be tailored to meet performance needs and complex design requirements) and hence widely used in the transportation industry.

9. Composites exhibit higher internal damping capacity

10. Composites have better dimensional stability over temperature fluctuations due to low coefficient of thermal expansion

11. Composites enjoy lower life cycle cost compared to metals

12. Composite parts can eliminate joints/fasteners, providing part simplification and integrated design compared to conventional metallic parts

13. Improved appearance with smooth surfaces

1.2 Glass fiber Reinforced Plastic(GFRP)

Glass fiber reinforced-plastic (GFRP) pipes are excellent candidates for transporting corrosive liquids due to their superior corrosion resistance, higher strength-to-weight ratio, low coefficient of friction, and lower maintenance cost compared to conventional steel pipes. There have been many studies on the suitability of thermosetting resin based pipes with glass reinforcement for various applications including water desalination [2], chemical and process industry [3], and oil and gas industries [4]. In the oil and gas industries, for example, SHELL had more than 600 km of epoxy-based GFRP piping installed by 1990 with 37% of the piping used for onshore hydrocarbon flow lines. SHELL had 10 years successful experience with pipe diameters smaller

than 150 mm where the highest pressure used was 95 bar and the maximum temperature was up to 65^0C. Significant cost savings were obtained in comparison with carbon steel when considering corrosion protection cost [5]. A more recent study in 1999 indicated that SHELL have over 2250 km of FRP piping in service [6].

1.2.1 Fiber Reinforcement

A fiber is an important constituent in a composite. Because of their excellent fatigue resistance, fiber reinforced composites have largely replaced metals and hence are being used in commercial fatigue-critical applications. A great deal of research has been carried out on the effects of fiber types, volume fraction, architecture, and orientations on the FRP's. The fiber generally occupies 30%-70% of the volume in the composites. The fibers can be chopped, woven, stitched, and/or braided. They are usually treated with sizing such as starch, gelatin, oil or wax to improve the bond as well as binders to improve the handling. The most common types of fibers used in advanced composites for structural applications are the glass, aramid and carbon. The glass fiber is the least expensive and carbon being the most expensive. The cost of aramid fibers is about the same as the lower grades of the carbon

fiber. Other high-strength high-modulus fibers such as boron are now being considered economically prohibitive.

1.2.2 Glass fibers

The most widely used reinforcement is glass fibers because of their low cost, high tensile and impact strength, lightweight and good corrosion resistance. Hence, vinyl ester resin reinforced with glass fibers represents a potential composite material for the oil and gas industry. The glass fibers are classified as E-glass, S-glass and C-glass. E-glass is designated for electrical use, S-glass for high strength and the C-glass is for high corrosion resistance. Of the three fibers, the E-glass is the most common reinforcement material used in civil structures and because of its good strength properties at low cost, it accounts for more than 90% of all glass fiber reinforcements. It is produced from lime-alumina-borosilicate, which can be easily obtained from abundance of raw materials like sand. The fibers are drawn into very fine filaments with diameters ranging from (2 - 13)$\times 10^{-6}$ m. The glass fiber strength and modulus can degrade with increasing temperature. Although the glass material creeps under a sustained load, it can be designed to perform satisfactorily at high temperatures. The fiber itself is regarded as an isotropic material

and has a lower thermal expansion coefficient than that of steel. Dejke et al [7] reports that glass fibers are known to degrade in the presence of water, and that moisture can decrease the glass transition temperature of the resin and act as a plasticizer, which may potentially have a significant effect on its flexural strength. It is important to note that E-glass fibers are themselves extremely susceptible to degradation in water and moist environments, and also in composite form.

The degradation of glass fibers due to environmental attack can severely affect the performance of GFRP laminates. The fibers in GFRP laminates are protected from the environment by the resin matrix. The degree of protection depends on the permeability of the resin from the environment and then the ability of the resin and interface to resist the pre mature cracking which would allow the environment into direct contact with the fibers.

1.2.3 Resin Systems

The resin is another important constituent in the composite. The two classes of resins are the thermoplastics and thermosets. A thermoplastic resin remains a solid at room temperature. It melts when heated and solidifies when cooled. The long-chain polymers do not chemically cross-link and hence are

undesirable for structural applications. Conversely, a thermosetting resin will cure permanently by irreversible cross-linking at elevated temperatures. This characteristic makes the thermoset resin composites very desirable for structural applications. The most common resins used in composites are the unsaturated polyesters, epoxies, and vinyl esters; the least common ones are the polyurethanes and phenolics. One of the important aspects to be considered in the durability issues of composites is the role of the polymer matrix. The primary role of the matrix in a composite is (a) to transfer stresses between the fibers, (b) to provide a barrier against an adverse environment, and (c) to protect the surface of the fibers from mechanical abrasion. Although its role in tensile load-carrying capacity is minor, it has a major influence on the inter-laminar and in-plane shear load transfer.

1.2.4 Vinyl ester Resins

The vinyl ester resin was developed to take advantage of both the workability of the epoxy resins and the fast curing of the polyesters. The vinyl ester has higher physical properties than polyesters and costs less than epoxies. The acrylic esters are dissolved in a styrene monomer to produce vinyl ester resins, which are cured with organic peroxides. A composite product

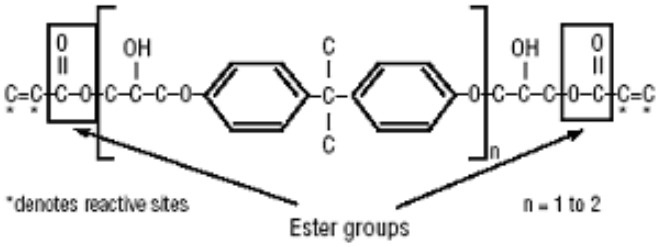

Figure 1.1: Idealized chemical structure of typical vinyl ester.

containing a vinyl ester resin can withstand high toughness demand and offer excellent corrosion resistance. The Figure 1.1 below shows the idealized chemical structure of a typical vinyl ester. As the whole length of the molecular chain is available to absorb shock loadings this makes vinyl ester resins tougher and more resilient than polyesters. The vinyl ester molecule also features fewer ester groups. These ester groups are susceptible to water degradation by hydrolysis illustrating that vinyl esters exhibit better resistance to water and many other chemicals than their polyester counterparts, and hence frequently used in applications such as pipelines and chemical storage tanks. Overall, the resin was chosen for its improved heat resistance, enhanced elongation, good corrosion resistance, and reduced emissions.

Vinyl esters based GFRP are generally preferred for moderate temperature applications in reinforced thermoset piping systems because of the fol-

lowing characteristics:

1. Improved corrosion resistance to strong acids, bases, and salt solutions up to a temperature of 93^0C

2. Improved impact resistance and greater tolerance to temperature and pressure fluctuations and mechanical shock than the polyesters

3. Excellent fiber wet-out and good adhesion to the glass fiber

4. Rapid curing and superior creep resistance

5. Vinyl ester based composites have demonstrated economy and better price to performance characteristics than steel and its alloys in many corrosive environments

6. Low maintenance requirements, design flexibility and ease of installation.

Vinyl esters cost a bit more than polyesters and so specific applications where vinyl- esters surpass polyesters include chemically corrosive environments (such as filament wound glass/vinyl ester chemical tanks) and in structural laminates where a high degree of moisture resistance is desired

1.2.5 Epoxy Resins

Epoxy resins are among the best matrix materials for many fiber composites. Epoxy resins are characterized by the presence of epoxide (or oxirane) functionality (Figure 1.2). It is an important industrial class of thermoset due to their chemical resistance, outstanding adhesive and good physical and mechanical properties. Epoxy resins adhere well to a wide variety of fillers, reinforcing agents and substrates. The chemical reaction between epoxy resins and the curing agent does not release any volatiles and water. It is also air curable, highly fillable, possesses low cure shrinkage, low susceptibility to stress formation. Epoxy resins are widely used for many important applications such as surface coatings, adhesives, reinforced plastics, printed circuit boards, etc. The large family of epoxy resins represents some of the highest performance resins of those available at this time. Epoxies generally out-perform most other resin types in terms of mechanical properties and resistance to environmental degradation. As a laminating resin, they have increased adhesive properties and are resistant to water degradation.

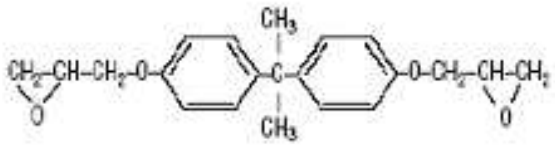

Figure 1.2: Idealized chemical structure of typical epoxy diglycidyl ether of Bisphenol-A.

1.3 Environmental factors affecting GFRP

Environmental conditions can promote brittle fracture in normally ductile plastics at levels of stress or strain well below those that could usually cause failure. The use of Glass fiber reinforced thermoset pipes is rapidly growing in applications such as potable water, seawater, sewage, and other corrosive fluid handling and transportation systems. In a majority of these cases, extended service lives under a harsh and changing environment are required with minimal maintenance. However, many of their potential applications remain unexploited due to a general lack of confidence in these materials to withstand the full range of environmental conditions. One of such potential applications is the use of GFRP thermoset pipes in the crude oil production and transportation piping networks. Inspite of extensive research that has been undertaken during the past 20 years, several major issues remain

unresolved regarding the performance of these materials under long-term exposure to environmental conditions, such as, seasonal changes in ambient temperatures, humidity, UV radiation, rain, salt water, precipitation of air borne contaminants, and other corrosive agents such as crude oil. The reliable engineering data on the effect of the full spectrum of environmental conditions on the mechanical properties of GFRP thermoset pipes, such as tensile, fatigue, flexural, impact, stress rupture, creep, fracture toughness, strain corrosion and hydrostatic properties are either scarce or unavailable. The interaction mechanisms of environmental conditions with the matrix and fiber phase are yet to be fully understood and properly characterized.

During the long-term environmental exposure of GFRP thermoset pipes, material degradation may occur in the matrix, fiber, and the fiber-matrix interfacial regions. The degradation rate may be constant or increase/decrease with time. The changes in the degradation rate may be gradual or abrupt. Changes in the degradation mechanisms may also occur during the course of long-term exposure. All of these issues raise serious concerns regarding the long term durability of the FRP pipes and constitute problems that require solutions before extensive use of the GFRP pipes can be made as a replacement to metallic pipes. It is the view of many design engineers,

manufacturers, and end users of GFRP pipes that without finding reliable answers with respect to these issues, many remarkable engineering and economic benefits that the GFRP pipes can offer may remain unexploited that may otherwise benefit the oil industry.

During past 30 years, large number of studies have been undertaken to investigate the effect of environmental exposure on the physical and mechanical properties of thermosetting resin based GFRP pipes. Many studies on GFRP degradations are reported in the literature, which include degradation due to corrosion, erosion, weathering, fatigue, moisture, fire, impact,temperature. In general, there are four major environmental factors which are most influential in polymer degradation. These are: (a)Temperature, (b)Water Absorption, (c) UV radiations and (d)Oxidation.

1.3.1 Temperature

It is well known that temperature has strong effects on mechanical properties of polymers. When temperature is increased, energy continues to be added to the polymer chains, and eventually doubly bonded C atoms begin to break and convert into single bonded. This leads to chain cleavage and crosslinking. This crosslinking occurs especially when the thermoset polymer is not fully

cured after processing [8]. This chain cleavage and crosslinking embrittle the polymer matrix and thus lowers the mechanical strength of the composite. Large temperature differential may also introduce sufficiently large stresses and may induce micro cracking, which in turn reduce the stiffness of the composite. These micro cracks increase permeability and water ingression through fiber/matrix interface and finally contribute to the degradation processes.

1.3.2 Moisture Absorption

Pipes are often in contact with water either due to weathering by rain or by carrying moisture containing fluids and chemicals. Moisture has potentially degrading effect on matrix materials. Vinyl esters contain the ester group in their molecular chain which is susceptible to hydrolysis of the side group, and may lead to cross-linking [9]. Moisture in many of its acidic, basic, neutral forms are known to affect the durability of composites. Moisture can penetrate all organic materials by a diffusion controlled process or by instantaneous absorption until the equilibrium moisture concentration is attained. Usually the moisture concentration increases initially with time and finally approaches the saturation point (equilibrium), after several days of exposure

to humid atmosphere. The time to reach the saturation point depends on the ambient temperature and the thickness of the composite. Drying can reverse the process but may not result in complete attainment of original properties. The uptake of water by polymer composites in general follows the generalized Fickian law of diffusion.

$$(\partial c/\partial t) = \quad D(\partial^2 \mathrm{c} \ / \ \partial \mathrm{x}^2) \tag{1.1}$$

Where c is the concentration, which is a function of time (t) and x (distance through the material) and D is the diffusion coefficient.

Absorption of water by resin in some instances may change the resin properties including the glass transition temperature through hydrogen bonding for the water molecules. Even though it is believed that glass fibers can be damaged by prolonged exposure to water, the most commonly used E-glass fibers contain only small amounts of alkaline-metal oxides, and so are resistant to damage by water.

1.3.3 UV Radiation

Another important degradation factor is the exposure to the UV radiations. The increased use of fiber-reinforced vinyl ester composites in outdoor applications has led to questions concerning the environmental durability of these materials, particularly to UV exposure.While much of the sun's high-energy radiation is absorbed by the atmosphere, some radiation in the 280 to 400 nm (ultraviolet) range reaches the Earth's surface. Since the energy of this radiation is 100 to 72 kcal, it is sufficiently strong to cleave covalent bonds and cause embrittlement due to cross-linking, which is considered to be the predominant reaction [10]. Although cross-linking is a useful reaction in making poly(vinyl ester) materials dimensionally stable at high temperatures, there may be undesirable consequences when it occurs after the materials are in service. The modulus increases with cross-linking, but the energy-absorbing capability goes through a maximum and decreases thereafter. A rubbery polymer system generally becomes brittle as a result. Another typical pattern accompanying cross-linking is a decrease in compatibility, so that plasticisers exude, system shrinks and delamination occurs [11].

1.3.4 Oxidation

The oxidative degradation of an organic polymer generally proceeds through free-radical reactions. Free radicals are formed by the thermal or photolytic cleavage of bonds. The radicals then react with oxygen to yield peroxides and hydro peroxides. Such reactions lead to both chain cleavage and to cross-linking. Cross-linking can be visualized as resulting from the combination of radical sites on adjacent chains [12]. Many synthetic organic polymers are oxidized in contact with the atmosphere. At room temperature in the absence of light the reaction may be very slow. But at elevated temperatures or during exposure to UV light the rate of oxidation is often quite rapid [13].

Vinyl esters-based GFRP is generally preferred for moderate temperature applications because of its:

1. Improved corrosion resistance to strong acids, bases, and salt solutions up to a temperature of 93^0C.

2. Improved impact resistance and greater tolerance to temperature and pressure fluctuations and mechanical shock than the polyesters

3. Excellent fiber wet-out and good adhesion to the glass fiber

4. Rapid curing and superior creep resistance.

The most widely used reinforcement is glass fiber because of its low cost, high tensile and impact strength, lightweight, and good corrosion resistance. Hence, vinyl ester resin reinforced with glass fiber represents a material for potential application as for pipe lines in the oil and gas industry. The potential cost savings associated with replacing steel pipes with FRP pipes with vinyl esters are considerable. However, the log term durability of these pipes is an important concern from the point of view of the end-users. FRP pipe suppliers may overestimate their maximum allowable temperature and pressure service conditions and often underestimate the effects of long-term service environment on the mechanical properties. Hence, the issue of long term behavior and aging of FRP pipes must be appropriately addressed before extensive use of FRP pipes in transporting organic liquids such as crude oil. The issue of long term durability becomes more critical especially when contaminants such as water, H_2S and chemically active solvents that are present with the crude oil. Therefore, long-term FRP material degradation is an imperative concern to the manufacturer and the end-user.

1.4 Fatigue Behavior of GFRP

Most failures of composite structures can be attributed to fatigue. Due to the heterogeneity of composite material at different scales, a large variety of interacting mechanisms contribute to fatigue failure. Microscopic investigations have shown that the transverse cracks are initiated from coalescence of fiber-matrix debonds, both in static and cyclic loading [14].

Representations of fatigue failure seem to have suffered most from the tendency to extend isotropic, homogeneous material concepts to anisotropic, heterogeneous ones. In metallic materials, fracture under cyclic loading is known to result from the initiation and subsequent growth of a single dominant flaw. Fatigue failure in composite laminates, however, involves combination of several micro and macro damage modes including matrix cracking, delamination, and fiber fracture (Figures 1.3 & 1.4). The order in which each type of damage occurs may vary depending on the constituent materials and stacking sequence. In deliberately tailored laminates where delamination and fiber fracture are suppressed, matrix cracking still takes very complex forms, involving sequential initiation and accumulation of multiple cracks in off-axis layers.

Components and structures manufactured from glass fiber reinforced plas-

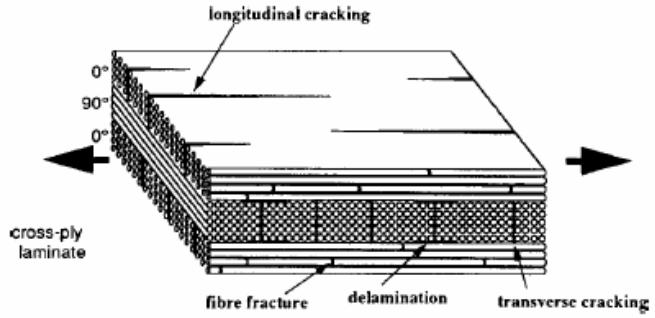

Figure 1.3: Different mechanisms induced in cross-ply laminates

tics (GFRP) are used increasingly in situations, where fatigue loading is present. Unfortunately GFRP is sensitive to fatigue loading unlike their high fiber modulus and more expensive counter part, Graphite/Epoxy fiber composites. The behavior of GFRP composites under fatigue loading is more complex than that of metallic materials because there are many more factors (both material and testing variables) that influence the fatigue crack growth including the matrix material, fiber material, volume fractions, fiber-orientation, moisture content, porosity, applied stress and strain rate.

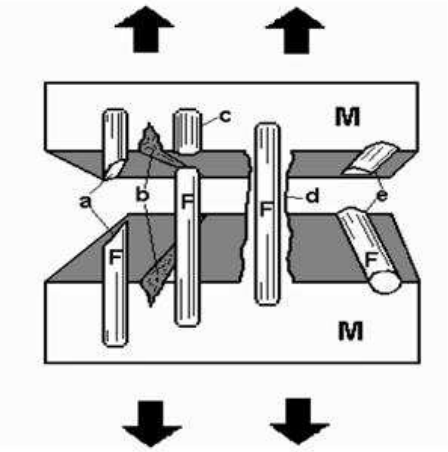

Figure 1.4: Failure types of fiber reinforced systems

1.5 Fractogrpahy of GFRP Composites

In fiber reinforced composites, the fatigue damage is a complex phenomenon characterized by initiation and multiplication of cracks, and is still an important research topic and far from being properly understood. Fractography can provide important information on location of fracture origins, direction of crack propagation, interactions with the crack front, crack development sequence, and the stress state at the time of fracture. Fracture markings include, but are not limited to, fracture origin, arrest lines, fracture mirror, twist, wake, and hackles, scarps, gull wings. Each of these features gives unique information about the failure mechanism of the material being inves-

tigated.

Just as in metals, it can be assumed that failure in a fiber composite emanates from small, inherent defects in the material. These defects may be broken fibers, flaws in the matrix and debonded interfaces.

When different plies of a laminate are placed with different orientations and bonded together, the response of those plies to any load component in a given direction is different. Clearly, plies which offer least resistance to loading and fail first are subcritical elements and plies offering most resistance to loading fail last and are the critical elements in the laminate.

In a more specific sense, subcritical elements usually contribute matrix and interface damage initiation and growth, while the critical elements usually undergo degradation involving matrix and fiber damage and control the final fracture event [15].

If the tensile components of loading are present the sequence of damage development usually starts with the formation of matrix cracks in the off axis plies. As the fatigue cycling continues, a characteristic pattern of matrix cracks forms i.e a stable pattern of regularly spaced matrix cracks develops in each off axis ply which has sufficient tensile stress to initiate matrix cracking. when matrix cracks are present, local interface cracks frequently form at ply

boundaries where the matrix cracks terminate. As cyclic loading progresses, localized splitting, delamination and fiber fracture develops in the plies.

1.6 Organization of Thesis

The rest of this thesis is organized as follows. Chapter 2 provides a detailed review of research work so far undertaken to investigate the issue of the environmental effects on glass fiber composites. Chapter 3 provides various mechanical testing methodologies and also the test plan for various exposures. Experimental results of the mechanical testing and the SEM fractography study are provided in Chapter 4 and their detailed discussions were presented in Chapter 5. Finally, conclusions and possible future directions of work are given in Chapter 6.

Chapter 2

Literature Review

This chapter provides a review of the research work undertaken by different researchers on the characterization of environmental degradation of GFRP pipes. In section 2.2, the effect of temperature and in section 2.3 effect of moisture on the mechanical properties of GFRP were discussed. Section 2.4 discusses the mechanical effect when epoxy is chosen as a matrix material. At the end of this chapter, a summary of the literature is included which is followed by the objective of the current study.

GFRP composites may last many years before showing signs of wear or degradation. However, they can deteriorate when exposed to sunlight, smog, acid rain, hot and cold temperatures, and long-term exposure to, or

immersion in, ocean water. Seawater exposures, either salt fog or oxygen-rich salt water, have been shown to result in the most severe degradation of material properties.

A large number of investigators have explored the effect of various environmental conditions on the physical and mechanical properties of glass fiber reinforced thermoset polymers. A wide range of environmental conditions, such as effects of temperature, UV radiations, seawater, hygrothermal aging, moisture, corrosive chemicals, and their influence on various mechanical and physical properties such as, tensile strength, fatigue, creep-rupture, impact, flexural strength, weight gain, glass transition temperature, and other polymer matrix properties have been explored. Reinforced thermoset piping systems include four primary resin groups: vinyl esters, unsaturated polyesters, epoxies, and furans.

Hammami et al [16] evaluated the durability and environmental degradation of Glass fiber Vinyl ester composites when exposed to high temperature, moisture, seawater and corrosive fluids. Long periods of immersion, in the corrosive fluid may form blisters, which may start growing by swelling pressure until final collapse. Combined action of water and corrosive fluid, matrix expansion and pitting may occur. Specimens immersed in seawater, uncured

chemical agents were easily leached out, leaving fiber s with no protection and will contribute to poor performance of specimens. Specimens exposed to high temperature and fully saturated environments were subjected to degradation caused by water diffusion through matrix

Chin et al [17] characterized the chemical and physical changes in polymeric matrix resins like vinyl ester following exposure to UV radiation, moisture, temperature and high pH environments. No significant changes were observed in tensile and hydrostatic strength for vinyl ester resins following immersion in water, salt solution and surface oxidation was observed. The most severe degradation was observed to take place in alkaline and saline environments.

Mahieux et al [18] presented a unique set of experimental data on the long-term oil immersion effects on various carbon fiber reinforced thermoplastic composites. The Teflon-based composite showed significantly altered behavior despite no changes in weight. Immersion in water was found to degrade the stiffness of the composite but not Tg and concluded that oil contact was responsible for the drastic degradation in the Tg for Carbon reinforced composite.

According to Brndsted et al [19], fatigue loading is often the limiting de-

sign factor as it causes premature microstructural damage, which contributes to the strength degradation of the component and eventually leads to failure. During the fatigue lifetime, a global degradation or damage of the material appears as micro cracks in the matrix material, interfacial cracking between fibers and matrix and fibers bundles, slipping in interfaces, and fiber failure. These failures will accumulate and raise the local stresses to approach the material strength which leads to local fatal failures. This degradation of the material can be monitored by measuring continuously the change in stiffness, using cyclic stress-strain data.

Ho Sung Kim [20] studied the fatigue mechanisms and lifetime prediction of E-glass/vinyl ester composites. Un-notched multi-directional composites subjected to tension-tension sinusoidal loading with a frequency of 1.5 Hz. Quantitative damage data was analyzed for the fatigue life prediction. S-N curves were constructed and fatigue mechanisms at different stress ranges in terms of stiffness reduction/fatigue modulus and quantitative damage was expressed. The micro-crack density increased logarithmically with increasing number of loading cycles. A model based on the fatigue modulus reduction was developed to predict an S-N curve using phenomenological parameters. The lifetime predictions were in good agreement with experimental results.

Bank et al. [21] reviewed the technical literature on the subject of environmental exposure (chemical and thermal nature) effects to determine the long term performance of various FRP's. Exposures such as temperature, moisture and chemicals in liquid solutions or in gaseous mixtures were included. The effects included the changes related to degradation of composite materials. Synergistic effects of mechanical load and exposure were also reviewed.

2.1 Effect of Temperature

The effect of temperature and relative humidity on the performance of glass reinforced composites is phenomenal. The dependence of moisture and temperature diffusivity is represented by Arrhenius relationship as

$$lnA = \quad lna + fln(x_0) - E/RT \tag{2.1}$$

Where A is rate coefficient, E is activation energy (ev), R is Universal Gas constant and T is Temperature.

Liao et al.[22] reported that higher the temperature and the longer the exposure time, the larger is the decrease in strength and modulus of Fiber

Reinforced Plastics (FRP) exposed to various fluids. They also observed that the tensile strength, compressive strength and modulus of GFRP degraded upon exposure to various moist and aqueous environments.

Signor [23] studied the chemical and mechanical properties, due to the effects of ultraviolet radiation exposure on vinyl ester. In this work, artificial ultra violet exposure was carried out using an integrating sphere based UV exposure chamber. The degradation was shown to be limited to a thin surface layer. Bulk mechanical properties like tensile strength along with strain and toughness of the material were greatly affected. A transition from slightly ductile to brittle behavior was also observed.

Liau [24] studied the individual and combined effects of ultraviolet light and thermal shock on the physical properties of polymer matrix composites in air and in a near vacuum system. They observed that the irradiated surface of the composites is the significantly damaged by UV. Weight loss increased with irradiation time, and the damage was higher when specimens were exposed in air than in the near vacuum system.

Study by Jungk et al. [25] showed a change in both fatigue strength and slope of the normalized S-N curve with response to change in temperature in vinyl ester/E-glass composites. The results showed an 8% decrease in

strength and an increase in slope from 7.5 to 12 % fatigue strength per decade of life between 0^0 and 65^0 C.

2.2 Effect of Moisture and Water

It is important to clarify that mass uptake due to immersion in liquids can occur through both absorption and adsorption. While the former is a bulk effect, the latter can be considered a surface effect. Absorption occurs through capillary uptake through voids, microcracks and interface gaps, resulting in the filling of free space without immediate plasticization or swelling [26]. In contrast the process of adsorption generates heat and results in swelling. In the case of polymers (and their composites) which inherently contain defects both processes are likely and hence the term moisture uptake to represent the combination of these processes is more appropriate.

Moisture absorption in composite materials is influenced by many factors. The nature and distribution of voids in composite materials dictate the volume of moisture it can retain. The presence of voids in the composite also has the effect of increasing the equilibrium moisture concentration and the diffusion coefficient. In most cases fiber diffusivity is negligible as compared

to that of the matrix.

The type of resin used becomes the key factor in characterization of moisture absorption in composite materials. Since moisture absorption is mostly a resin-dependent phenomenon, resins such as epoxies are known to absorb moisture under different factors depending on their chemical structure. Typically, vinyl ester resins possess lower maximum moisture content than epoxy matrix resins. Moisture diffusion is known to be temperature dependent. The famous Arrhenuis equation incorporates this dependence

$$D_t = \quad D_{z0} exp(-E/RT) \tag{2.2}$$

where D_t is the Diffusion Coefficient in m^2/s, E = Activation energy (cal/g-mol), R = Universal gas constant (1.987 cal/g-mol-K), T = Absolute temperature (K), D_{z0} = Temperature independent diffusion coefficient in mm^2/sec.

Micro-cracks in composites allow the absorption of more moisture due to the capillary action of the voids; leaching through these voids might decrease moisture retention.

McBagonluri et al [27] highlighted the effects of short-term cyclic mois-

ture aging on the quasi-static strength and fatigue tension-tension (R=0.1) performance of a glass/vinyl ester pultruded composite system in both fresh and salt water. The quasi-static tensile strength reduced by 24% at a moisture concentration of 1% by weight. This reduction in strength was not recoverable, suggesting that the exposure to moisture caused permanent damage in the material system. The fatigue damage evolution and subsequent failure of fiber-reinforced composites have been found to be independent of moisture content or moisture regime in the short term, although long-term aging and moisture ingress appear to affect the fatigue performance of the material.

Srivastava et al [28] indicated that water penetration into polymer matrix composites involves three mechanisms: (i) diffusion of water molecules into the matrix directly and to a much lesser extent, into the filler material, (ii) flow of water molecules along the filler matrix interface, followed by diffusion into the bulk matrix, and (iii) transport of water through micro cracks or other forms of micro damage, such as pores or small channels already present in the material or expanded by water.

Langmuir-type diffusion is reported to explain the penetration of water in polyester and vinyl ester resins. The Langmuir model considers two phases of water, bound and unbound. Plasticization, swelling stress, hydrolysis,

debonding and formation of cracks are the possible occurrence of environmental exposure and which should also influence the diffusion of water in the material [29]. Moisture wicking along the fiber-matrix interface degrades the interfacial bond strength, resulting in loss of microstructural integrity.

Kin Liao et al. [30] have studied the long-term durability of the glass fiber vinyl ester composite coupons in various moist environments (5 and 10 % salt solutions, de-ionized water). They found that long-term environment fatigue behavior is not controlled by the quantity of water absorbed rather governed by combination of both load and the fluid environment. they observed that the flexural strength and the modulus decreased with the environmental ageing.

Springer [31] investigated the effects of environment on glass fiber reinforced polyester and vinyl ester composites immersed in liquids and in humid air and found that the weight loss and changes in material tensile strength depend on the temperature and environment.

Karbhari et al. [32] characterized the mechanical response of E-glass/vinylester composites immersed in de-ionized water, seawater, and synthetic seawater. They observed a discernible difference in response between samples immersed in sea water and deionized water, with the former causing a greater level of

fiber-matrix debonding and outer-layer degradation, resulting in increased degradation of the tensile performance, and the latter causing faster diffusion up to the midplane, resulting in more severe drops in the interlaminar shear strength. Drying of specimens, even over prolonged periods, does not result in complete reversal of the tensile strength of the material.

Karbhari et al. [33] exposed E-glass/vinyl ester samples to fresh water, seawater, cold, and freeze-thaw conditions.They found decrease in mechanical characteristics such as tensile strength, modulus and glass-transition temperature and concluded that the sea water exposure to be most detrimental. The presence of moisture/solution has a significant effect; both in terms of physical and chemical aging and in terms of micro cracking and fiber-matrix debond initiation [34]. It was shown that degradation due to alkali exposure is more severe than exposure to the deionized water. Data from accelerated tests is used to provide long-term predictions, which are shown to correlate well with experiments in the short-term.

Kootsookos et al [35] investigated the durability of glass fiber/vinyl ester composite when immersed in the seawater at a temperature of 30^0 for about 2 years. Four point bend load flexural tests were conducted on specimens exposed to sea water immersion for different time periods. Considerable

amount of moisture absorption as well as the chemical degradation of the matrix and fiber/ matrix interfacial region occurred due to immersion. This resulted in degradation of about 30% and 40 -50% in flexural modulus and strength respectively for the vinyl ester based composites. Despite the superior chemical stability of vinyl ester based composites over the polyester type (the quantity of leached organic species was lower) in sea water immersion, the flexural properties degraded to a similar extent to that of polyester materials.

Sampath [36] et al. studied two fiber-reinforced polymer composites for susceptibility to degradation when exposed to aggressive environments. Composites and fibers were then exposed to a mixed inoculum of aerobic bacteria and to an anaerobic sulfate reducing bacteria. Fiberglass-reinforced vinyl ester and isophthalic ester composites, as well as the individual glass fibers, were extensively degraded due to the bacterial attack. The composite samples underwent degradation in the form of fiber pullout, as well as matrix cracking, leading to subsequent reduction in the mechanical properties.

Hai C. Tang et al [37] conducted the fatigue experiments under various environments: air, fresh water, saltwater at 30^0C and investigated the temperature effects on fatigue life of E-glass/vinyl ester composite when sub-

merged in seawater. They observed that the fatigue life was reduced by two orders of magnitude as temperature increases from 4^0C to 65^0C. They also observed 25% and 32% reduction of the ultimate strength in fresh water and salt-water conditions, respectively, as compared to the dry conditions. The corresponding reduction in tensile modulus was reported to be 15% and 11% respectively.

2.3 Epoxy Composite as a Pipe material

Beckry et al [38] investigated the combined effects of load, moisture and temperature on the properties of E glass / epoxy composites. Preliminary results indicated that the tensile modulus and tensile strength were affected by the presence of moisture and mechanical loading when compared to control specimens. For shorter durations of exposures at room temperature, slight increase of about 5% in strength and slight decrease (11%)in modulus were observed; whereas at longer exposure durations, a noticeable reduction was observed. For specimens conditioned under stress in water at 65^0C for 1000 hours exhibited reduction of about 18% and 28% in tensile strength and modulus respectively.

Fernand [39] investigated the effects of moisture absorption and exposure to elevated temperature on the mechanical properties of glass fiber reinforced epoxy composite tubes. Filament wound tubular composite specimens were immersed in distilled water at two different temperatures for approximately four months and their moisture absorption was recorded. The rate of moisture absorption was greater for the group of specimens immersed in distilled water at an elevated temperature (50^0C) than those at room temperature (20^0C). The author reports that the strength and stiffness decreased to some extent with the exposure to moisture and at (50^0C). Microscopically, the greatest water damage was apparent in the matrix, fiber-matrix interface. It was found that there was less resin adhesion to the fibers with increasing water temperature. Fiber strength was lowered possibly due to either leaching out of the glass fibers interface layer or glass fiber embrittlement, and less effective bonding and load distribution at the fiber-matrix interface.

Environmental exposure results in reduced interfacial stress transmissibility due to matrix plasticization, chemical changes and mechanical degradation. Matrix plasticization reduces matrix modulus. Chemical degradation causes hydrolysis of bond. Mechanical degradation is the outcome of matrix swelling strain. An interfacial reaction may induce various morphological

modifications to the interphase at the fiber/polymer interface [40].

The solubility and kinetics of moisture transport mechanisms were investigated over a range of partial pressure and temperature by Marsh et al. [41]. They studied moisture adsorption and diffusion into epoxy and epoxy-glass composites and demonstrated that solubility follows Henry's law. The diffusion is best described as non-Fickian.

Exposure to elevated temperature can result in degradation of mechanical properties, cracking, chalking and flaking of polymers [42]. The first form of damage in laminated composite is usually matrix microcracks. These microcracks are transverse to the loading direction and are thus called transverse cracks. Matrix microcracks cause degradation in properties in composite laminates and also act as precursors to other forms of damage leading to laminate failure [43]. Delamination is a critical failure mode in composite structure. The interfacial separation caused by the delamination may lead to premature buckling of laminates, excessive intrusion of moisture and stiffness degradation. While in some cases a delamination may provide stress relief and actually enhance the performance of a composite component [44].

Vauthier et al. [45] analyzed the effects of hydrothermal aging on the fatigue behavior of a unidirectional glass/epoxy composite. In the first stage,

the fatigue property of the un-aged composite was studied in various environments involving moisture and temperature. Local interactions between the surrounding moisture and the crack tip was found to induce significant losses in lifetime at the highest elevated temperature (70^0C). In the second stage, fatigue properties were investigated after a preliminary aging step. Hygrothermal defects created in the bulk composite during the water-sorption step induced a significant decrease in fatigue properties, especially after immersion aging. A strong correlation was found between the physico-chemical degradation of the matrix and the fiber weakening.

Monney et al [46] studied the mechanical behavior of an epoxy-glass composite under photo-oxidation and concluded that the conjugated actions of the mechanical stress due to photo-oxidation and of the temperature accelerate the weakening of the material by cracking at the surface and thus making the material weak externally as well as internally.

Kwang Bok Shin [47] exposed the graphite/epoxy composite material to both natural environments for 5 years, and accelerated environmental conditions including temperature, ultra violet radiation, and moisture for 2000 hours to evaluate the degradation of the mechanical and physical properties. Decrease in strength and stiffness of the material was observed for both the

natural and accelerated environmental conditions. He predicted an accelerating factor for long-term performance of the material.

2.4 Fractography of Composites

Damage mechanisms in composite laminates subjected to fatigue loading consist of events which cause initiation, growth and localization of damage with subsequent failure if cyclic loading is continued. This damage usually initiates at the subcritical elements of the laminate causing the local stress redistributions, accelerated degradation of the critical elements, local damage accumulation and strength reduction [48].

Mandell [49] noted that fatigue failure, in general, is characterized by the progressive accumulation of cracks in the matrix and at the matrix/fiber interface, resulting in loss of strength and stiffness. This progression in remaining strength values reach a limiting point where it equals the cyclic stress and, consequently, failure results. This general trend in failure does not explicitly apply to tensile failure in glass reinforced composites, where failure appear to be either a fiber- or a strand-dominated phenomenon, and it is independent of matrix type or interface.

Mandell [50] and co-workers investigated effect of fatigue due to fiber orientation, fiber volume fraction, resin type, and glass fiber type on the fatigue resistance of polymeric composites. Mandell [51] also observed a trend in fatigue strength degradation rate of 10% of the initial ultimate tensile strength per decade of fatigue cycles(10% UTS/decade) and was characteristic of the fatigue behavior of glass-fiber reinforced polymeric-matrix composites. The fatigue failure of the glass-fiber composite seems to occur as a result of gradual deterioration of the load-bearing fibers, and is independent of fiber volume fraction, resin type, glass fiber type and fiber orientation.

The fatigue behavior of composites has also been shown to be highly dependent on the stress ratio, R and the frequency of applied cyclic load,f [52]. Mandell and Meir [50], Elyn and El-Kadi have discussed the effects of R on the fatigue life of composites and have shown that for a given maximum stress in a tension-tension case ($-\infty < \mathrm{R} < 1$), the fatigue life of the composite increases with increasing magnitude of R. Also Scharpery [53], Mandell and Meir [50] Saff and Sun and Chan [54] have shown that by increasing f, the fatigue crack propagation rate decreases and in doing so there is an increase in fatigue life of polymer provided that the increase in temperature is small.

Boller [55] investigated the effect of matrix materials on the fatigue

strengths of glass reinforced plastic laminates. Foye and Baker [56] observed that when positions of the plies in a [±15 / ±45] laminate were changed, a 10^6 difference in fatigue strength of about 25000 psi occurred. Whitney [57] made similar observations on the influence of stacking sequence on the fatigue strength and failure mode of composite laminates. Amijima [58] studied the influence of glass content on the fatigue properties of glass fiber composites.

A strong interface displays an exemplary strength and stiffness but is very brittle in nature with easy crack propagation through the interface. A weaker interface reduces the stress transmissibility and consequently decreased strength and stiffness. A crack here is more likely to deviate and grow at the weak interface. It results in debonding and/or fiber pull-out and contributes to improved fracture toughness [59].

A composite material may contain randomly spaced microvoids, incipient damage sites and microcracks with statistically distributed sizes and directions. Therefore, the local strength in the material varies in a random fashion. The failure location as well as degree of damage induced in the material will also vary in an unpredictable mode. Therefore, the mechanical and fracture behavior can be strongly influenced by the loading rate, temperature and

material microstructure [60].

For multidirectional laminates, delaminations tend to grow from the edges and influence the subsequent accumulation of damage. Hence, the fatigue process becomes dependent on the specimen width, and does not reflect an intrinsic material behavior [61]. Broutman and Sahu [62] proposed a theory that loss of strength is a product of the difference between static and fatigue strength and the applied load cycles : expected fatigue life ratio.

2.5 Objective of the Present Study

The main objective of this proposed study is to investigate the effects of environmental conditions on the performance and durability of glass fiber reinforced vinyl ester and epoxy based thermoset composite pipes intended for crude oil transportation. The study will focus on the investigation of effects of exposure on the fatigue and the tensile properties under both natural and the accelerated environmental conditions. This study also undertakes a fractographic examination of the fracture process to help understand the mechanism involved in the fracture of the GFRP pipes under various mechanical and environmental conditions.

Chapter 3

Experimental Procedure and Exposure Periods

This chapter describes the experimental program which is designed to achieve the objectives of this study. This includes description of material of study and specimen preparation, plan for various exposures,and the methods used for mechanical testing. Section 3.1 deals with the material and sample preparation, 3.2 with various test exposures which includes both natural and accelerated conditions. In Section 3.3, mechanical testing procedures including both tensile and fatigue are explained.

3.1 Material and Sample Preparation

The material used in these experiments is a filament wounded glass fiber vinyl ester composite. In the present study, a ±[54.5] glass fiber vinyl ester composites were used. A ±[54.5] winding angle satisfies both the circumferential (hoop) and longitudinal (axial) strength requirements of most pipes and pressure vests, usually manufactured by the filament winding process. The samples for environmental exposures and for subsequent fatigue and the tensile testing were in the form of rings which was machined from GFR/Vinyl ester and GFR/Epoxy pipes. These pipes were obtained from local manufacturer. The pipes 150 mm internal diameter with 6mm wall thickness were provided in 10m lengths. Single side double notched specimens 12 mm thick were made using a diamond cutter. Figure 3.1 shows a typical sample.

3.2 Environmental Exposures

3.2.1 Natural Exposures

1. Outdoor exposure

2. Crude Oil Exposure

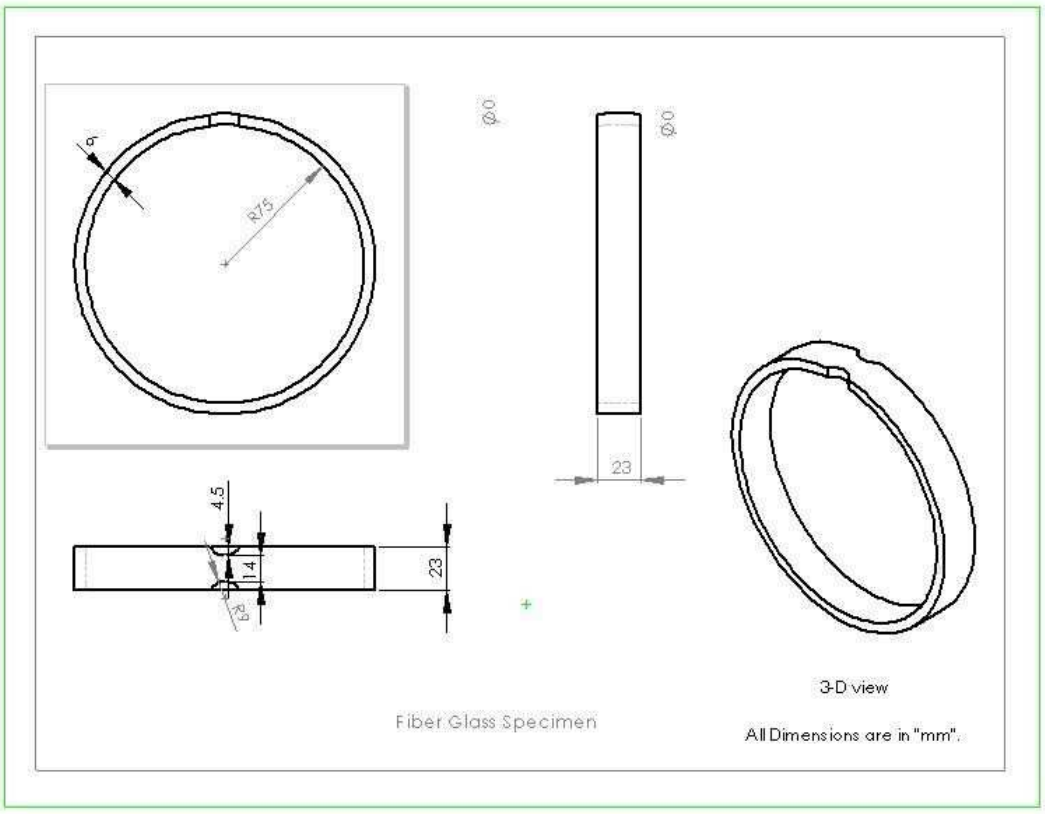

Figure 3.1: Ring Specimen

3. Sea water immersion

Natural (Outdoor) environment exposure site available at KFUPM campus was selected for natural exposure. For outdoor exposure condition, specimens used were of ring type. Pipes about 160 mm length made from GFRV1 pipes is used for Crude oil exposure condition. The pipes were mounted on the six test racks as shown in the Figure 3.2. Care has been taken that the pipes should not get disturbed or damaged and were monitored regularly. Environments mimicking field conditions include prolonged outdoor exposure of test samples and pipes segments filled with crude oil.

For sea water immersion exposures, the special frames were designed and fabricated from CPVC plates. Each frame was capable of holding fifteen 1.25m long GFRV1 pipes. These frames were then submerged in the Arabian Gulf sea water at a distance of approximately 200 m from the KFUPM Beach shore line.

3.2.2 Accelerated Exposures

Accelerated exposure tests can usually reach the same degradation as natural exposure tests, but K times faster (where K is the acceleration factor) assuming a linear rate model as indicated in ASTM E 632 (Standard Practice for

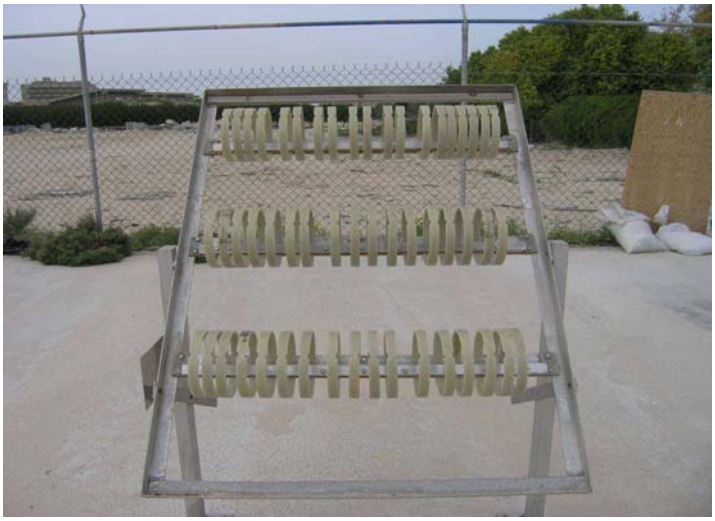

Figure 3.2: Outdoor exposure

Figure 3.3: Outdoor exposure filled with Crude Oil

Developing Accelerated Tests to Aid Prediction of the Service Life of Building Components and Materials). For conducting the accelerated exposures, the GFRV2 material was selected and the specimens were exposed for various exposure times ranging from 300 hours to 3000 hours. Various accelerated exposures, which utilize acceleration by using higher temperatures, more severe aggressive conditions, and moist conditions were considered. These exposures included the following

1. Dry Heat (40^0C and 70^0C)
2. Salt Water Spray
3. Humidity (Ambient and 100%)
4. 100% Oxygenated Salt water immersion
5. UV Radiation Exposure

These conditions were used to simulate outdoor exposures to heat, air oxidation, ocean spray, intense sunlight. The temperature and humidity was varied and controlled in the appropriate tests chambers. The oxygen-saturated saltwater test was a modification of a system reported for the photo-oxidation of plastics. Accelerated exposure tests can usually reach the

same degradation as natural exposure tests, but K times faster (where K is the acceleration factor) assuming a linear rate model as indicated in ASTM E 632.

Dry Heat

The effect of dry heat on materials is important in operations using composites in a desert region, such as the Saudi Arabia. LBB Series Despatch oven has been used for dry heated exposure. This oven has an efficient forced heated air circulation to maintain a constant temperature. The oven uses an microprocessor based digital controller that maintains the actual chamber temperature to the desiring level. Ring specimens were hung using PVC pipes as shown in the Figure 3.4.

Due to the harsh climatic conditions of the Gulf region, the specimens were also tested at higher temperature of 70C. Similar to the Dry heat 40^0C, the ring specimens were also kept in a separate oven at 70^0C for various durations as shown in Figure 3.5.

Figure 3.4: Dry heat 40^0C exposure

Figure 3.5: Dry heat 70^0C exposure

Salt Water Spray

Salt spray exposure testing was designed to provide a controlled, Salt fog environment. This test has been used extensively to provide relative corrosion or deterioration resistance data. Continuous salt spray exposures are widely specified for testing components and coatings for corrosion resistance.The apparatus used a Q-Fog CCT 600 model as shown in the Figure 3.6. The test temperature was set to 95^0F (35^0C) and salt fog was introduced. A 3.5% wt. salt solution was continuously atomized into the chamber. The pH was measured at room temperature after collection of the condensate and followed procedures stated in ASTM B 117 (Standard practice for operating Salt Spray apparatus).

Humidity Condition

Humidity also plays a very important role in the degradation of the composite pipes. During the humidity function, the chamber is maintained at 100% relative humidity by forcing hot water vapor into the chamber. Singleton Corrosion Test Cabinet model DIN FJ32H1-N-N-23 as shown in the Figure 3.7 is used for the exposure of the pipe to humidity for both the ambient and 100%. Humidity testing manual ASTM D 2246-65 (reapproved 1981) (or) D

Figure 3.6: Salt spray exposure

2247-86a was followed for the carrying out the exposure tests.

Oxygenated Salt Water Immersion

The reaction rate (between oxygen and hydrocarbon based plastics) can increase as a function of the amount of oxygen available (e.g. 100% instead of 20% in air), and also the reaction rates can double for each -7^{0}C increment above room temperature (21^{0}C). When glass reinforced polymers are exposed to air (20% oxygen), they gradually deteriorate over many years, due to chemical reactions between the polymer and the oxygen.

The high oxygen-salt-water exposure tests were carried out in test cham-

Figure 3.7: 100% Humidity exposure

bers built from plastic tanks Figure 3.8. Four tanks each 50 gallon capacity were used and were half filled with sea water. Oxygen was supplied continuously in form of compressed air. Supports were designed and built to hold the composite rings in submerged salt water. Periodic inspection of the tank was done to check the level of oxygen using a oxygen meter.

UV Radiation

Ultra violet radiation exposure chambers (UV chambers) are the primary means for generating laboratory weathering data for a wide range of polymeric composites. The UV radiation spectrum comprises wavelengths of

Figure 3.8: Oxygen-Salt water immersion

Figure 3.9: Oxygen-Salt water immersion

between 290 to 400 nm, which corresponds to energies of between 415 to 300 kj/mol. These energies are in the same range of many organic compounds. This environmental chamber will offer a temperature control between 0C and +100C, and relative humidity of 0 - 100 %. For conducting the UV tests, a Q-Sun Xenon test chamber which is a laboratory simulator for the damaging effects of weathering. It is used to test the relative humidity of materials. This chamber can produce damage that might occur over months or years of outdoor exposure. The conditions for accelerated UV exposure are as follows: UV Filter - DAYLIGHT : Q; UV sensor - 340 nm; Irradiance : 0.68 W/m2; Humidity : 10 The damage effects of sunlight are simulated using the xenon lamps. The exposure was done as per the ASTM D 4329 (Standard Practice for Operating Light and Water Apparatus Fluorescent UV and Condensation Type for Exposure of Plastics).

3.3 Mechanical Testing

For conducting the mechanical experiments, two universal testing machines were used, i.e. Instron 8801 and Instron 5569.

Figure 3.10: Ultra violet radiation exposure

3.3.1 Tensile Testing

Tensile testing was performed on the Instron 5569 tensile testing system. Test system control, data collection and analysis are performed by Instron's Bluehill software. The machine is equipped with an environmental chamber that allows testing at non-ambient temperatures. The experimental setup is shown in the Figure 3.11

Apparent hoop tensile strength of the pipes was determined by the split disk Method (ASTM D 2290-00). The test fixture involves two half disk shaped components which were attached to the upper and lower connecting arms of the test fixture with pins. Split-disk test specimens were located between the two half disk shape components and the upper and lower connecting arms, with the reduced sections aligned perpendicular to the plane of separation of the two half disk shape components Figure 3.13. The test method allows determination of the apparent tensile strength utilizing a split disk test fixture. An apparent tensile strength rather than a true tensile strength is obtained in this test because of a bending moment imposed during testing at the split between the split disk test fixtures. The test fixture is designed to minimize the effect of this bending moment. The tensile tests were conducted at a cross head speed of 0.3 mm/min. The test specimen was

a full-diameter, full-wall thickness rings cut from the exposed pipe sections. A minimum of 3-4 specimens were tested for each condition. The apparent or the ultimate tensile strength is calculated as following

$\sigma_a = (P_b/2)/(A_m)$

where P_b is the maximum load A_m is the minimum cross sectional area

3.3.2 Fatigue Testing

Fatigue testing was performed on 8801 Instron machine. Instron 8801 is a closed loop servo-hydraulic single axis fatigue testing system. The main controlling modes of the system are strain (10 %), load (100 kN) and position (75 mm) with a frequency range from 0 to 200 Hz. The photograph of testing frame is shown in Figure 3.12. The machine is equipped with a hydraulically actuated self-aligning gripping system. To ensure the vertical alignment of the specimen specially machined inserts were used during the tests. Any pre-loading induced during clamping was adjusted to zero prior to testing by the re-calibration of the load cell after clamping.

The ring specimens and the split-disk fixture described previously was used for fatigue testing. Results of the fatigue tests are typically presented as a plot of applied stress (S) against number (N) of cycles to failure. The

Figure 3.11: Instron 5569 machine

ordinate is generally the stress or strain amplitude or the maximum stress or strain in a cycle and is plotted on a linear scale. The abscissa is the number of cycles to failure for a fixed stress cycle and is plotted on a logarithmic scale. The stress levels chosen for fatigue testing will be based the design pressure. The fatigue tests were done in tension/tension mode with a stress ratio(R) of 0.1 at a frequency of 10 Hz under ambient conditions and the loading levels chosen ranged from 20% to 50%.

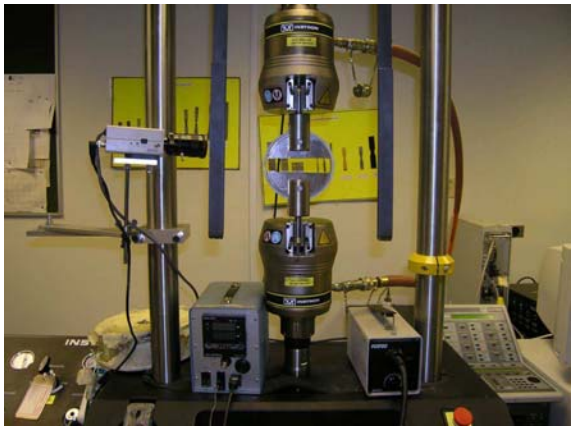

Figure 3.12: Instron 8801 machine

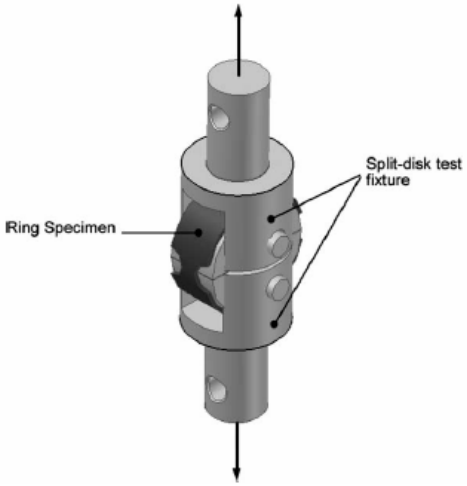

Figure 3.13: Split-disk fixture setup

3.3.3 Fracture Surface Analysis

The surface morphology of the damaged GFRP specimens were studied under both optical and the scanning electron microscopy to investigate the damage.

The fractured specimens were initially studied under the optical microscopy before the in depth analysis is done under SEM. The microscopic analysis was done using a Pixera optical microscope with a magnification range from 27X to 190X.

3.3.4 Scanning Electron Microscope

The fracture surface morphology of the failed specimens was studied using a Joel JSM Scanning electron microscope. The magnification range available is 35X to 300,000X. The excitation potential can be varied between 1 to 50 kV. To suppress charging and increasing electron emission, gold coating of the fracture surface was done. This process provided very fine uniform coating of a conducting material (i.e. gold), so that the surface after coating was an exact replica of the underlying material. The coating was done by vacuum depositing in several stages provided by rotary and diffusion pumps of Joel Fine Coat Ion Sputter JFC-1100 with a vacuum of 0.1 Torr at 1 - 1.5 kV. The time and amperage were selected with the constraint of the coat thickness

and the specimen surface area.

The specimens were reduced to the appropriate size (for mounting on SEM) by Buehler Isomet ^{TM} low speed saw using a diamond wafer, in order to eliminate the possibility of inducing any post fatigue damage near the fractured surface

Chapter 4

Experimental Results

This chapter presents the results of tensile and fatigue testing and their analyses.

Fatigue and tensile tests were conducted on both glass fiber reinforced vinyl ester composite pipes and glass fiber reinforced epoxy composite materials. Glass fiber reinforced vinyl ester pipes were supplied in two different batches. Vinyl ester based pipe materials are referred as GFRV1 (first batch) and GFRV2 (second batch) materials and the epoxy based materials as GFRE.

To generate reliable base line tensile data, several tests were performed on each material. Nine tensile tests were performed on the as received GFRV1

pipes and ten tests on as received GFRV2 pipes and six tensile tests on the as-received GFRE pipe material to determine the virgin material tensile properties.

For fatigue testing, 6-8 samples were tested for each exposure and the loading levels chosen ranged from 20% to 50% of the ultimate tensile strength. Results of the fatigue tests were represented as a plot of applied stress (S) against number (N) of cycles to failure.

The testing program continued throughout the duration of this work to determine the effects of outdoor natural exposure for a period ranging from 3 to 12 months and various accelerated exposure conditions for periods ranging from 300 to 10000 hours.

4.1 Tensile Test Results

Tensile tests were performed in accordance with the ASTM standard 2290 ("Standard test method for apparent hoop tensile strength of plastic or reinforced plastic pipe by split disk method"). The tests were conducted on GFRV1 composites exposed to outdoor conditions and on GFRV2 pipes exposed to accelerated conditions.

4.1.1 Outdoor Exposures

The tensile test results for the GFRV1 pipe material are depicted in Figure 4.1. The average base line tensile strength (apparent hoop tensile strength) and the modulus for the as received GFRV1 were 253 MPa and 3.2 GPa respectively. Table 4.1 provides the tensile test results for GFRV1 specimens exposed to the outdoor conditions in Dhahran for the periods of three, six and twelve months. Analysis of the result reveals that the exposure for 3 months has resulted in an increase in the tensile strength of GFRV1 from an average value of 253 MPa to 271 MPa, which is an enhancement by almost 7% (Table 4.1). A slight decrease in the average tensile strength after this enhancement at 3 months exposure was observed with strength approximating to 256 MPa at 12 months of exposure. Upto 6 months of exposure to natural outdoor condition, variation in the average modulus of the GFRV1 material was not observed (i.e around 3.2 GPa). However, for the 12 month exposure, the stiffness decreased by almost 47% from the baseline value (Figure 4.1) and also the elastic strain to fracture (e_f) increased significantly with decrease in stiffness. This decrease in stiffness may be attributed to a plausible plasticization of the matrix which may have occurred during the long term exposure of 12 months.

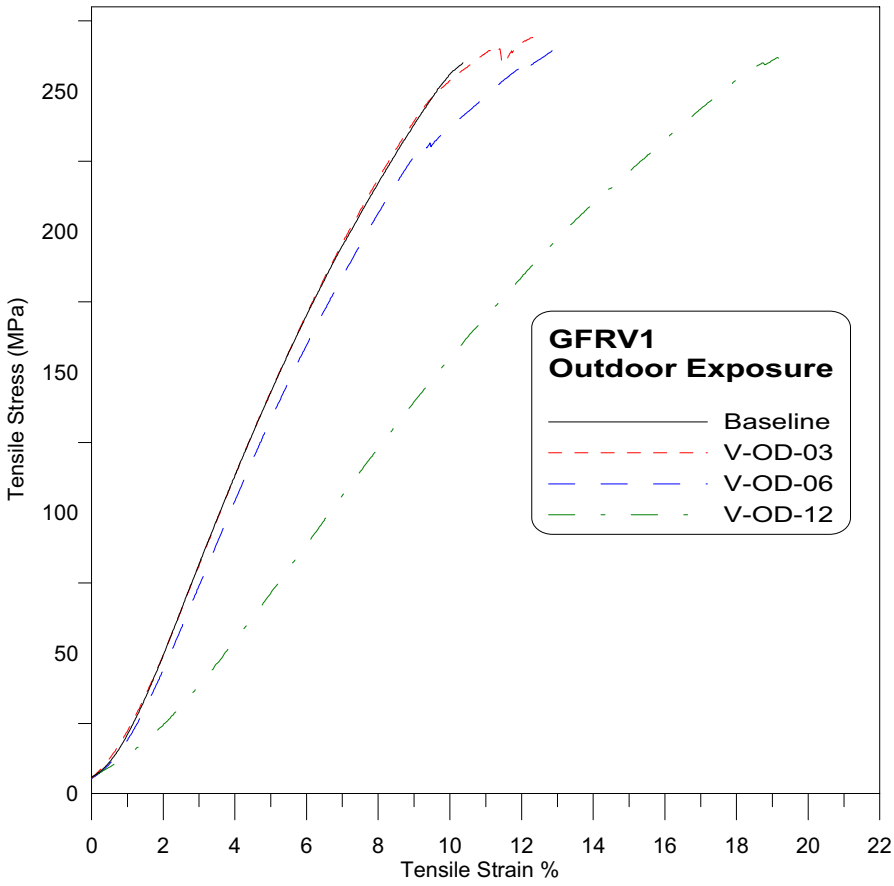

Figure 4.1: Tensile plot for outdoor exposure GFRV1 pipe specimens exposed to outdoor environmental conditions at KFUPM exposure site in Dhahran.

Table 4.1: Tensile properties for GFRV1 composite for natural outdoor exposure.

Exposure Duration (No. of samples)	**Avg.Tensile Strength (MPa)**	**Avg.Modulus (GPa)**	**Strain to fracture %**
Baseline (9)	253	3.2	11
3 Month (4)	271	3.2	12
6 Month (3)	259	3.1	13
12 Month (3)	256	1.7	19

Outdoor exposure of crude oil filled pipes

Pipes filled with crude oil were exposed to outdoor conditions (Figure 3.3). After exposure to various exposure periods, the ring tests specimens were obtained from emptied and cleaned pipes. Tensile tests were performed on these ring tests specimens. The results show an improvement in the tensile strength of the pipes filled with crude oil and exposed to outdoor conditions as seen in Figure 4.2. The average tensile strength increased from 253 MPa (Baseline) to 287 MPa (12 month exposure value) (Table 4.2). This improvement by about 13% in the tensile strength for the crude oil exposure was similar to the one observed in the outdoor exposure. However not much variation was observed in the average modulus values upto 12 month exposure for oil filled exposure. A slight improvement in the strain to fracture was noted with increase in the exposure time.

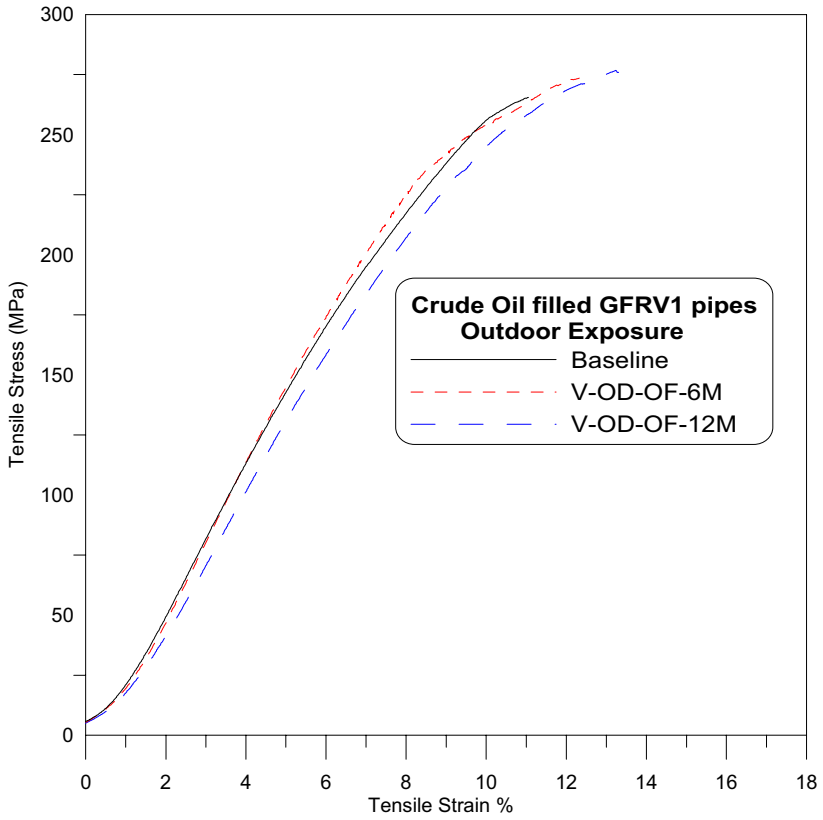

Figure 4.2: Tensile plot for crude-oil filled GFRV1 pipe specimens exposed to outdoor environmental conditions at KFUPM exposure site in Dhahran.

Table 4.2: Tensile properties for GFRV1 composite for natural outdoor exposure-oil filled Condition.

Exposure Duration (No. of samples)	**Avg.Tensile Strength (MPa)**	**Avg.Modulus (GPa)**	**Strain to fracture %**
Baseline (9)	253	3.2	11
6 Month Oil filled (3)	269	3.2	12
12 Month Oil filled (2)	287	3.2	13

Sea Water Immersion

The environmental durability of the pipes was evaluated by immersing the pipes in Gulf sea water for a period of 12 months. The exposed pipes were then machined to obtain ring test specimens and tensile tests were performed. Figure 4.3 shows the tensile test results for the sea water immersion condition. The results indicate an increase of about 6% in the tensile strength and about 10% decrease in the average modulus for 12 months of exposure (Table 4.3). A typical sample of the 12 month sea water immersed pipe is shown in Figure 4.4.

Figure 4.5 compares the tensile strength for GFRV1 composite pipes for various natural outdoor exposures.

Table 4.3: Tensile properties for GFRV1 composite exposed to Gulf sea water.

Exposure Duration (No. of samples)	**Avg.Tensile Strength (MPa)**	**Avg.Modulus (GPa)**	**Strain to fracture %**
Baseline (9)	253	3.2	11
12 Month Sea water immersion (2)	268	2.9	13

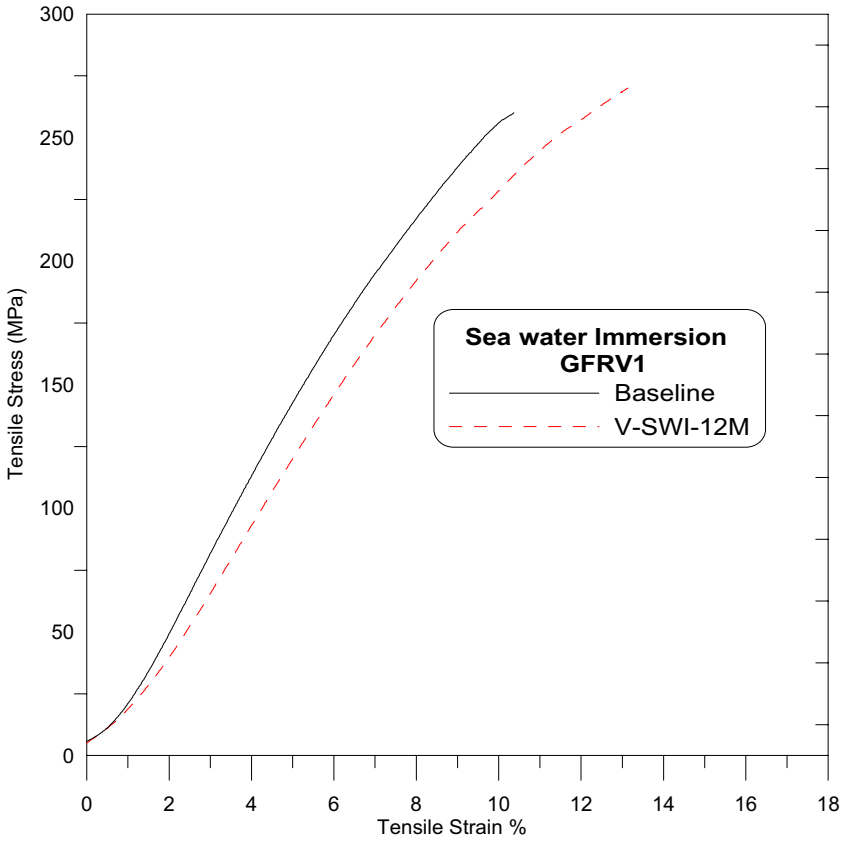

Figure 4.3: Tensile plot for sea water immersion GFRV1 pipe specimens exposed in Arabian Gulf.

Figure 4.4: GFRV1 composite when immersed in Arabian Gulf for 12 months

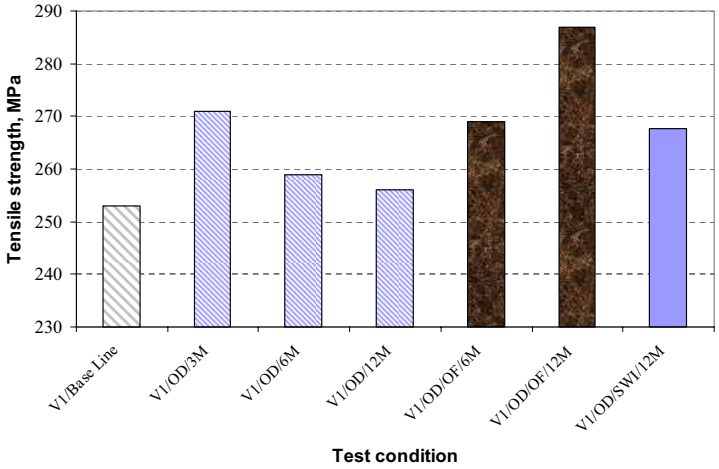

Figure 4.5: Comparison of tensile strength for GFRV1 for various natural outdoor exposures

Table 4.4: Average tensile strength values (in MPa) for GFRV2 for various accelerated exposures

Exposure Condition	**300 hrs**	**1000 hrs**	**3000 hrs**	**10000 hrs**
Baseline	203	203	203	203
Dry heat-40^0C	202	202	197	205
Dry heat-70^0C	221	195	217	218
Salt spray	202	206	190	173
100%Humidity	205	220	203	190
Humidity-Ambient	–	209	209	178
Oxygen-Saltwater	193	185	189	164*

* represents 6000 hours of exposure for OSWI.

4.1.2 Accelerated Exposures

Ring specimens obtained from GFRV2 pipes were exposed to various accelerated environmental conditions. Tensile tests were performed after each exposure for various time intervals.

The base line tensile strength of the received GFRV2 pipe material was found to be 203 MPa, which is almost 20% lower than the GFRV1 pipe material (253 MPa). The average modulus for GFRV2 was also much lower (1.75 GPa) than that of GFRV1 (3.2 GPa).

Dry heat Exposure

Table 4.4 shows the tensile test results for specimens exposed to dry heat at 40^0C. No noticeable effect on the tensile strength of the material was

Table 4.5: Average Modulus values for GFRV2 (in GPa) for various accelerated exposures

Exposure Condition	**300 hrs**	**1000 hrs**	**3000 hrs**	**10000 hrs**
Baseline	1.75	1.75	1.75	1.75
Dry heat-40^0C	1.53	1.63	1.79	1.78
Dry heat-70^0C	1.28	1.60	1.70	2.04
Salt spray	1.52	1.61	1.72	1.82
100%Humidity	1.47	1.55	1.60	2.04
Humidity-Ambient	–	1.76	1.73	1.80
Oxygen-Saltwater	2.63	2.73	1.53	1.56

Table 4.6: Average Strain to fracture (%)values for GFRV2 for various accelerated exposures

Exposure Condition	**300 hrs**	**1000 hrs**	**3000 hrs**	**10000 hrs**
Baseline	14	14	14	14
Dry heat-40^0C	13	14	13	14
Dry heat-70^0C	22	18	17	14
Salt spray	17	15	13	13
100%Humidity	16	17	15	14
Humidity-Ambient	–	14	14	13
Oxygen-Saltwater	10	9	14	14

observed at 300 and 1000 hours of exposure. The average value remained at 203 MPa (Base line tensile strength value). Even the longer time exposure of 10,000 hours did not seem to have caused any degradation in tensile strength. (Figure 4.6). Overall, not much variation was observed in tensile strength, modulus and strain to fracture values at 40^0C of dry heat.

Exposure to dry heat at 70^0C for 300 hours produced an improvement in the tensile strength by about 10% from 202.7 MPa to 221 MPa and stiffness lowered by 8%. This improvement in the average tensile strength was consistent at higher exposure periods i.e. upto 10,000 hours of exposure. The material begins to stiffen after 3000 hours of exposure. A 19% increase in the modulus value was noted for 10,000 hours of exposure. This improvement in the modulus suggests that embrittlement of the matrix occurs at high temperatures and longer exposure periods.

UV Exposure

For the UV exposure, the degradation in the tensile strength of the GFRV2 material started immediately with degradation in the tensile strength by 7% after as early as 100 hours of exposure and about 10% reduction even after 3000 hours of exposure (Table 4.7). From the tensile plot (Figure 4.8) it

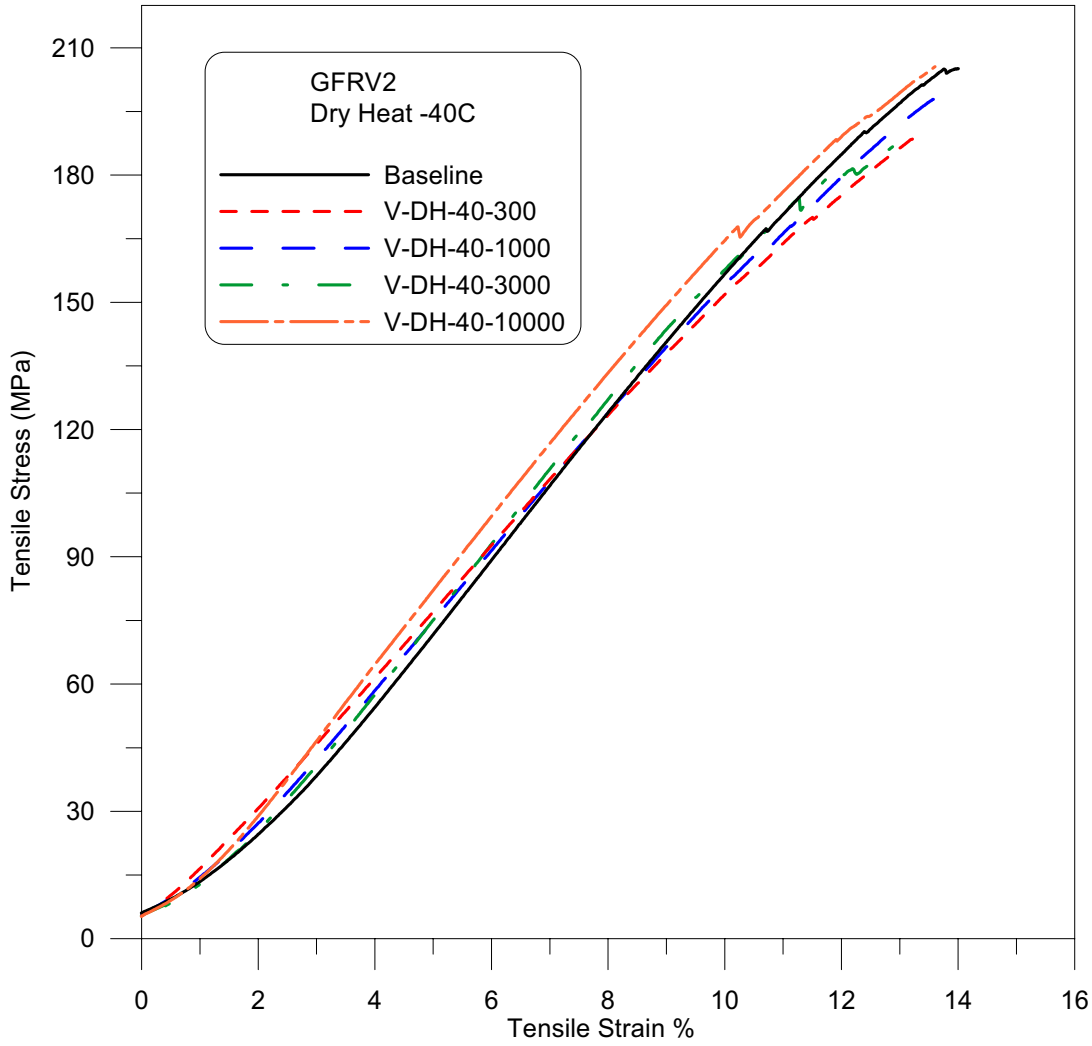

Figure 4.6: Tensile plot for accelerated exposure of GFRV2 exposed to Dry heat-40C condition

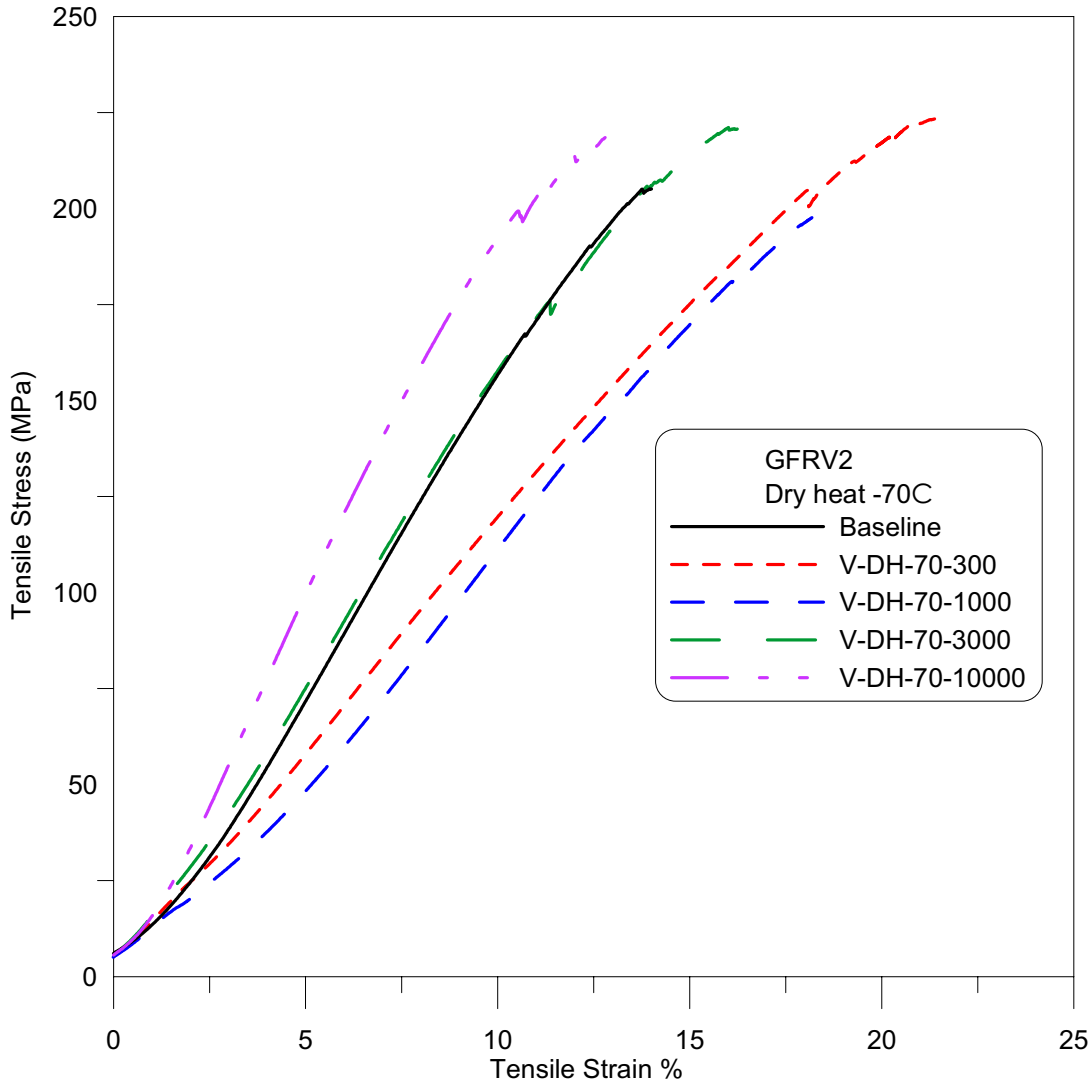

Figure 4.7: Tensile plot for accelerated exposure of GFRV2 exposed to Dry heat-70C condition

appears that the change in the stress-strain behavior curve upto 300 hours of exposure was insignificant. However with increase in the exposure time to 3000 hours, the composite appears to become slightly stiffer with modulus showing an increase by almost 14% from baseline value. This increase in the modulus value indicates that embrittlement of the matrix occurs with longer periods of exposure. A slight variation in the strain to fracture values was observed upto 3000 hours of exposure.

Table 4.7: Tensile properties for GFRV2 composite exposed to UV radiation

Exposure Duration (No. of samples)	**Avg.Tensile Strength (MPa)**	**Avg.Modulus (GPa)**	**Strain to fracture %**
Baseline	203.0	1.75	14
UV-100 hours	188.5	1.80	12
UV-300 hours	199.5	1.70	13
UV-500 hours	185.0	1.80	12
UV-1000 hours	185.0	1.86	12
UV-3000 hours	183.0	1.99	11

Humidity Exposure

The tensile test results for samples exposed to 100% humidity for 300, 1000, 3000 and 10,000 hours are also provided in Table 4.4. It can be observed from these results that there is presumably no significant effect of exposure on tensile strength of the GFRV2 material up to a period 3000 hours. This suggests that exposure to 100% humidity until a period of 3000 hours does

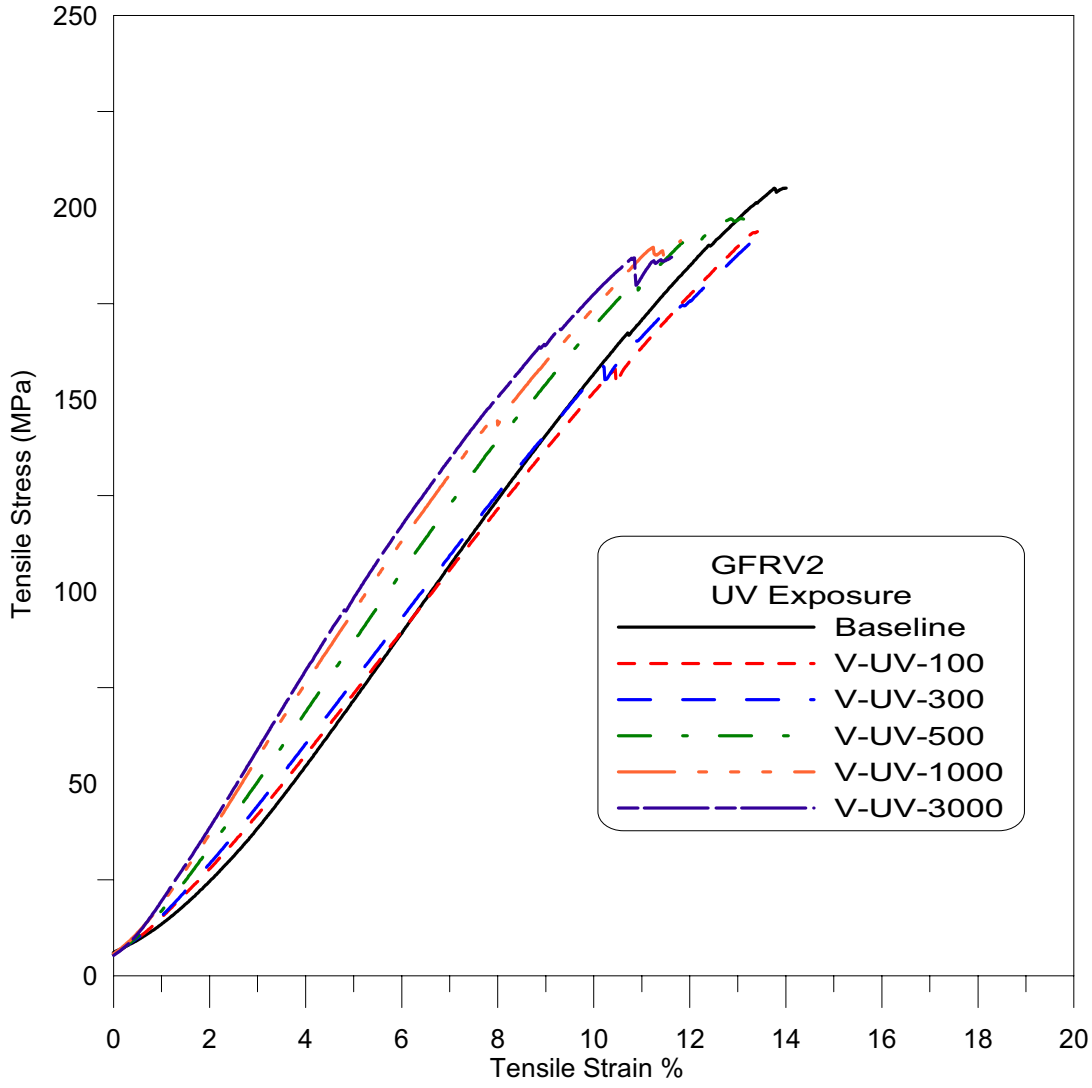

Figure 4.8: Tensile plot for accelerated exposure of GFRV2 exposed to UV Exposure

not induce any noticeable degradation in the material. After 10,000 hours of exposure, a 6% decrease in tensile strength is noted suggesting that the 100% humidity exposure begins to induce its detrimental effect after very long exposure periods of exposure.

Although the effect of 100% humidity exposure conditions did not produce any changes in the tensile strength of the composite until a period of 10,000 hours, the material did suffer a reduction in its stiffness rather quickly. The modulus decreased from 1754 MPa to 1472 MPa after 300 hour exposure to 100% humidity, this is almost a 16% reduction. After this initial decrease in the modulus, further exposure did not show any sign of further stiffness degradation. In fact a 17% improvement in the material stiffness was observed at 10,000 hours of exposure (Figure 4.9).

Apart from exposing the specimens to 100% R.H condition, exposure to ambient humidity conditions were also considered to evaluate the degradation effect. As expected, this condition does not seems to affect the strength of GFRV2 material with strength varying negligible until 3000 hours of exposure. However longer exposure period of 10,000 hours resulted in 12% decrease in the tensile strength of the material (Figure 4.10). The modulus variation was negligible even after longer exposure periods.

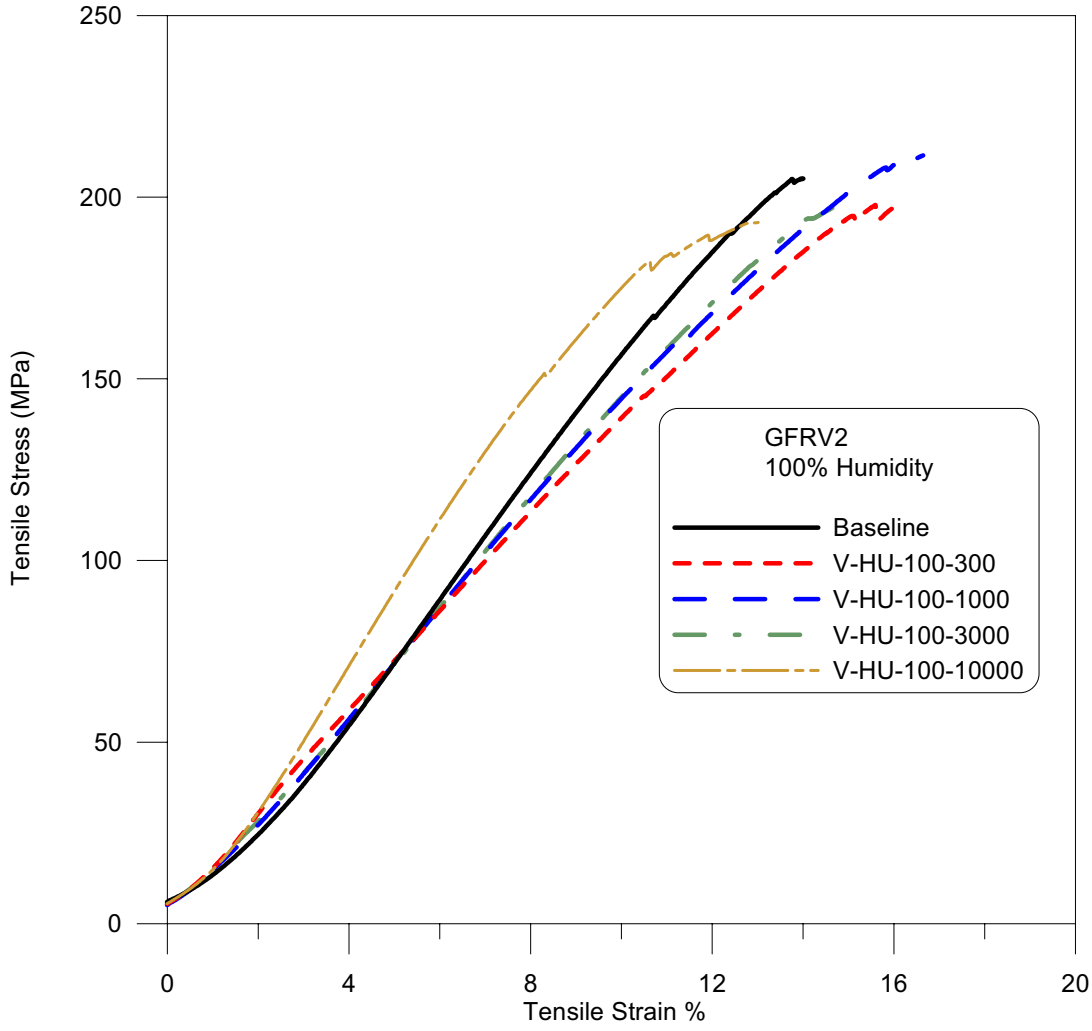

Figure 4.9: Tensile plot for accelerated exposure of GFRV2 exposed to 100% Humidity condition

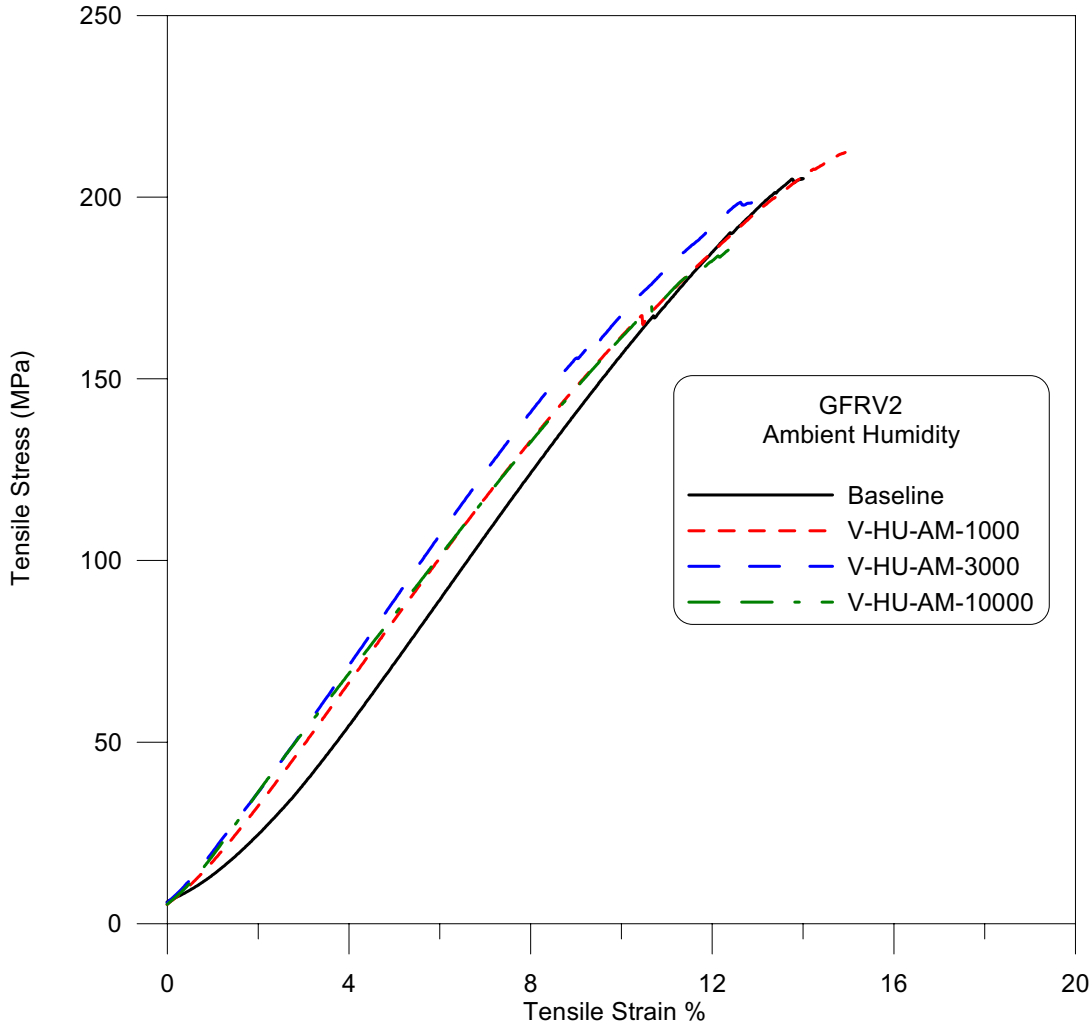

Figure 4.10: Tensile plot for accelerated exposure of GFRV2 exposed to Ambient humidity condition

Salt Spray Exposure

The exposure to salt spray at room temperature for 300 and 1000 hours did not produce any significant effect on the tensile strength of GFRV2 (Table 4.4). However, the salt spray exposure beyond 3000 hours produced a slight detrimental effect on the composite (about 6% reduction in tensile strength). After 10,000 hours of exposure a noticeable 15% decrease in tensile strength is noted suggesting that the salt spray exposure degrades the material more significantly at higher exposure periods. Maximum reduction in the modulus was observed for 300 hours (about 13%). After this initial decrease in the modulus, further exposure did not show any sign of further stiffness degradation. Rather a slight improvement in the material stiffness was observed at 10,000 hours of exposure (Figure 4.11).

Oxygenated salt water immersion Exposure (OSWI)

The oxygen-rich environments exhibited immediate degradation in the material showing an average 5% reduction in the tensile strength for 300 hour exposure. A noticeable reduction of 19% in the tensile strength was observed after 6000 hours of exposure whereby the tensile strength decreased from 202.7 MPa to 164.4 MPa.

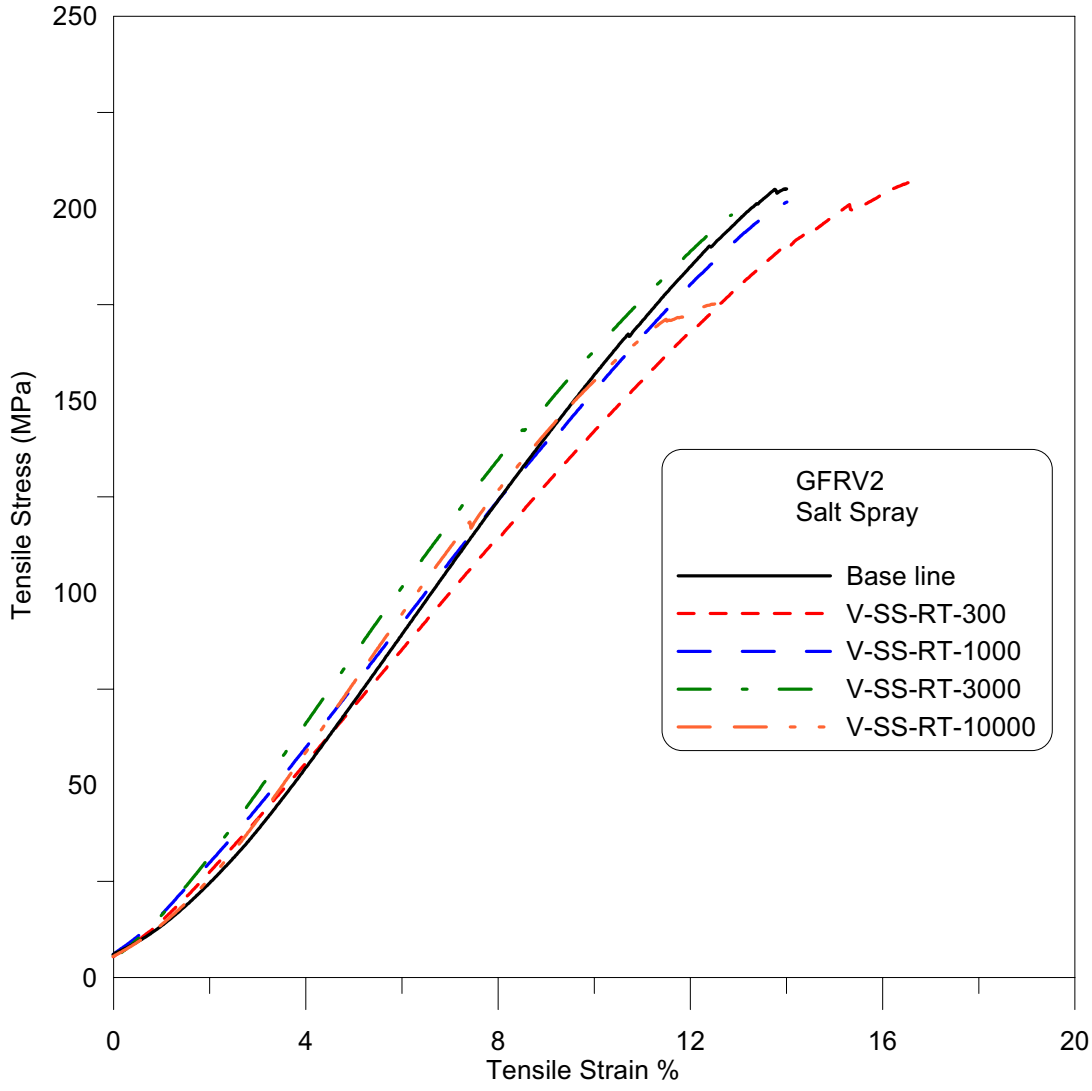

Figure 4.11: Tensile plot for accelerated exposure of GFRV2 exposed to Salt spray condition

There is also significant improvement in the modulus values for 300 and 1000 hours exposure to OSWI. The modulus increased from its baseline value of 1.75 GPa to 2.73 GPa at the exposure period of 1000 hours. However as the immersion time increased beyond 3000 hours, the modulus dropped sharply from its peak value of 2.7 GPa to 1.56 MPa which in fact brought the material stiffness to a level much lower than the baseline stiffness i.e. beyond the initial modulus value (Table 4.5).

A more general comparison of the effect of different accelerated exposure times on the apparent hoop tensile strength of the material exposed to various accelerated conditions is made by plotting the experimental results as bar charts as displayed in Figure 4.13. It is observed that in general, the accelerated exposures either degraded the strength or had little effect on the composite material.

Among the seven accelerated conditions under consideration, UV radiation and oxygenated salt water immersion proved to be the two most severe detrimental conditions as noted in 4.4 which is similar to the Jamond [63] observation.

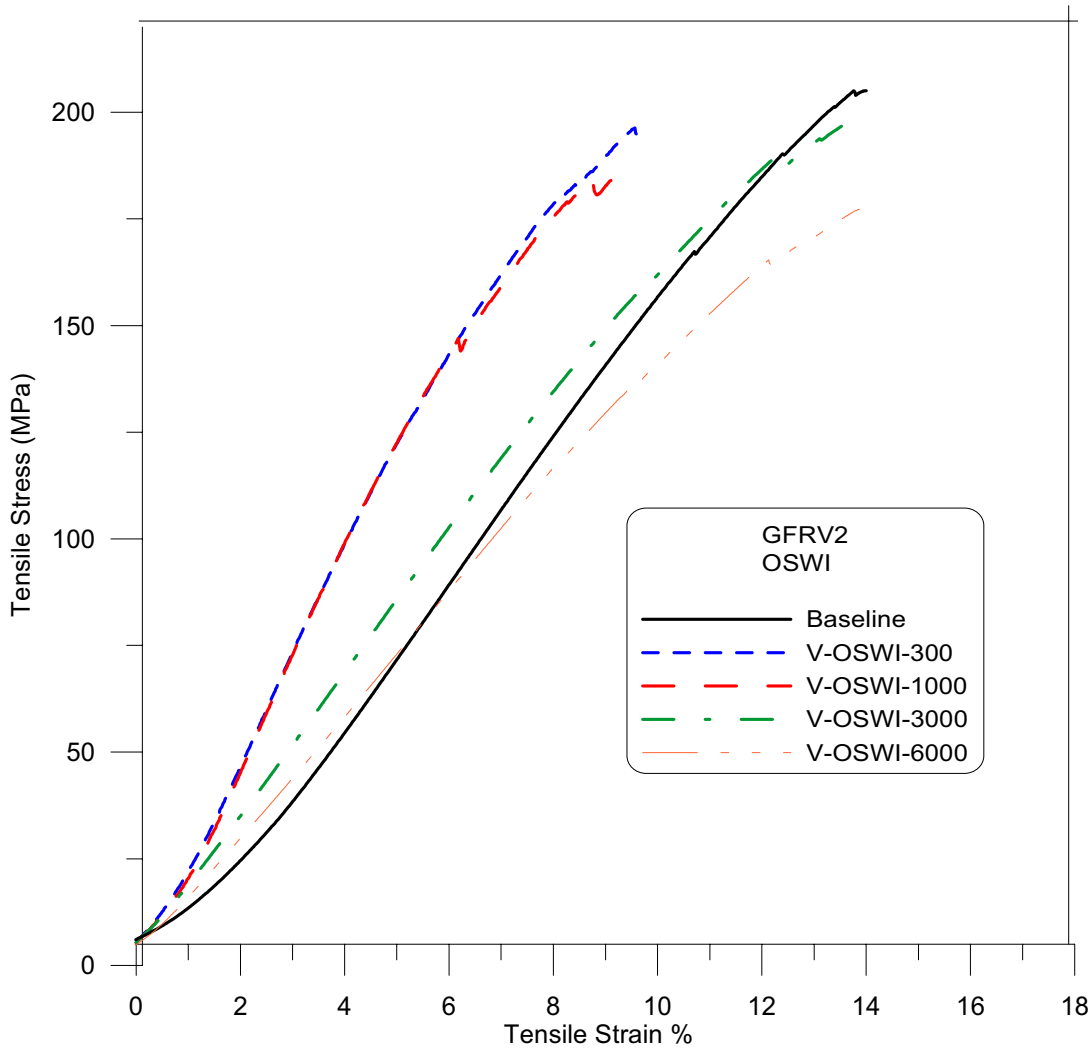

Figure 4.12: Tensile plot for accelerated exposure of GFRV2 exposed to Oxygen-Saltwater condition

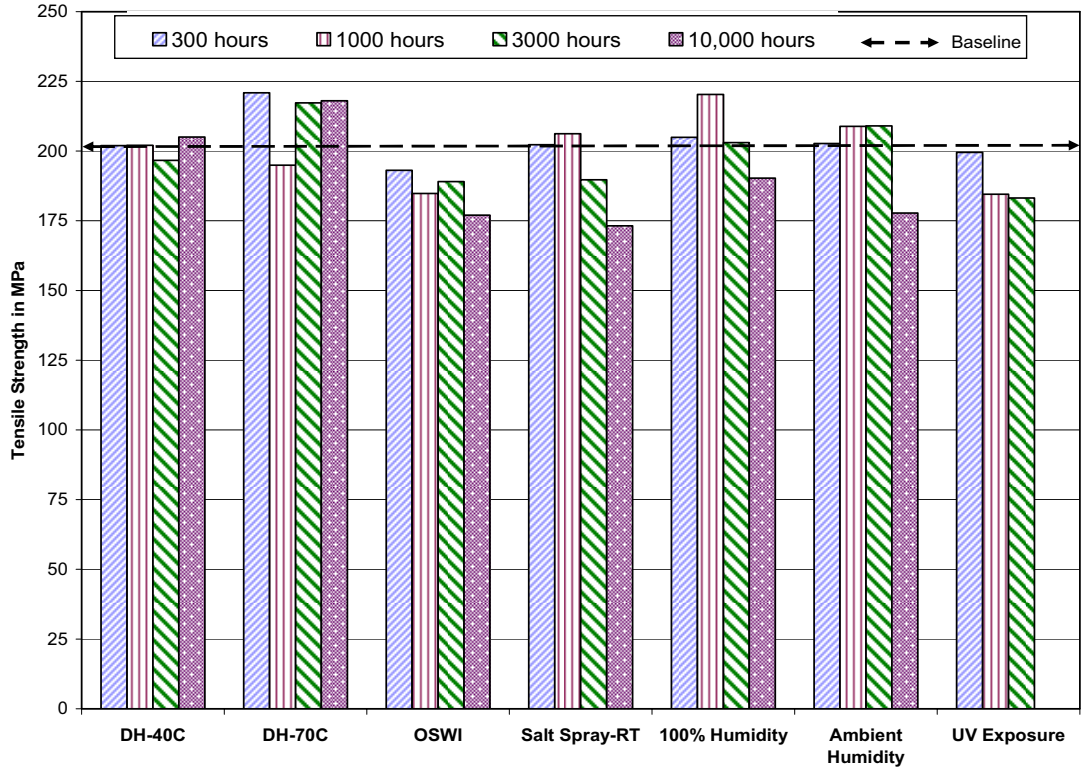

Figure 4.13: Comparison of average tensile strength for various accelerated conditions of GFRV2 for different exposure periods

4.1.3 GFRE Composite

For the GFRE composite pipes, the test results for the oxygenated salt water immersion are presented in Table 4.8. It is observed that the baseline mechanical properties of GFRE composites are superior to those of GFRV composites. The baseline strength of GFRE was approximately 327 MPa as against 253 MPa for GFRV1 material. This can be attributed to much higher cross link density and better compatibility of epoxy resin to glass fiber than that of vinyl ester resin.

For the GFRE composite, exposure to the oxygen salt water immersion caused lowering of the tensile strength by 9.5% from the base line value of 327 MPa for the 3000 hours of exposure. A 16% reduction in the strain to fracture values was observed after 3000 hours of exposure.A slight degradation of 7% in the modulus value was observed for 1000 hours Figure 4.14. However, this degradation was later compensated with increase in the exposure time (for 3000 hours) with modulus attaining the base line value. Therefore, it seems that the absorbed moisture has far greater effect on the tensile strength than on the modulus [64].

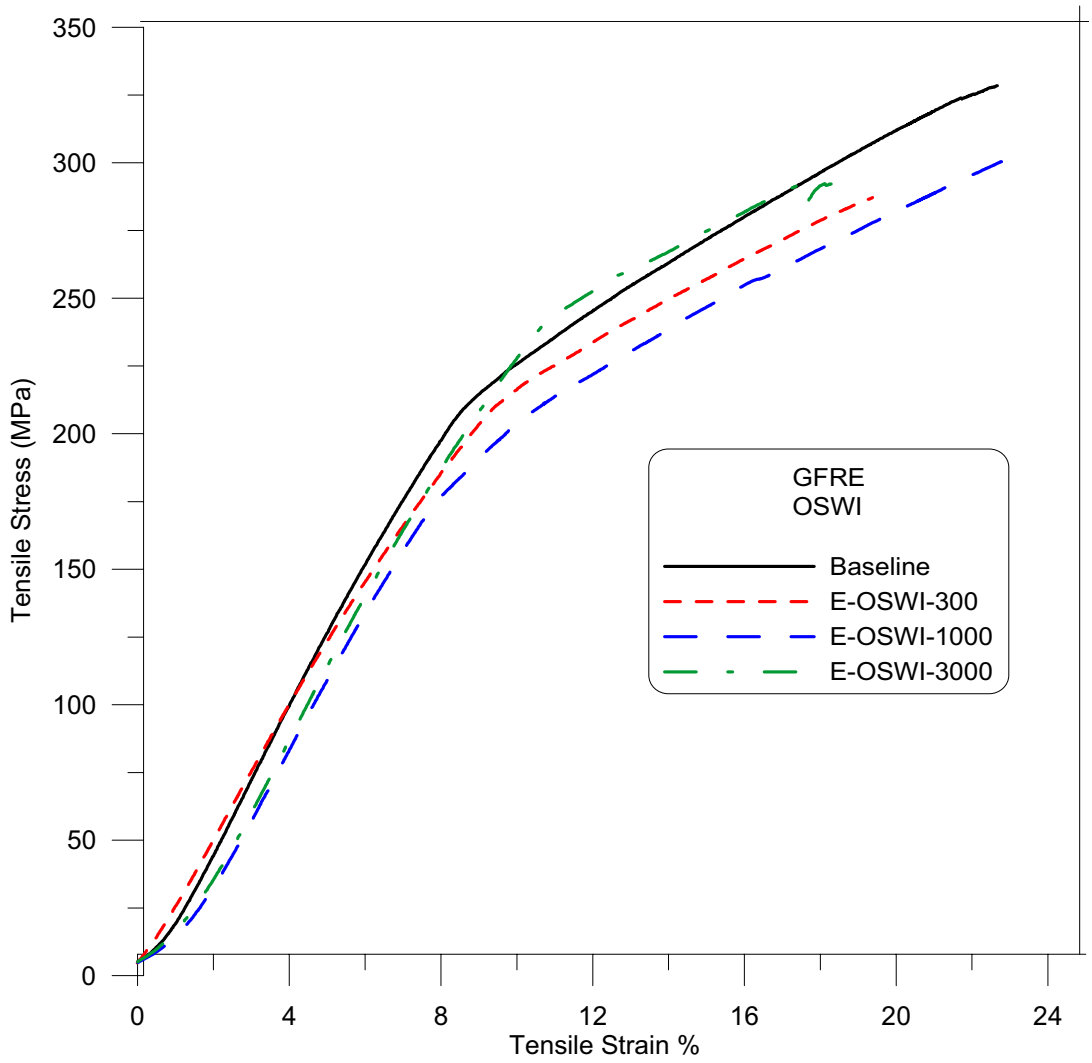

Figure 4.14: Tensile plot for accelerated exposure of GFRE composite exposed to Oxygen-Saltwater immersion

Table 4.8: Tensile properties for GFRE composite exposed to OSWI

Exposure Duration (No. of samples)	**Avg.Tensile Strength (MPa)**	**Avg.Modulus (GPa)**	**Strain to fracture %**
Baseline (6)	327	2.7	2.2
OSWI-300 hrs (3)	292	2.6	2.0
OSWI-1000 hrs (2)	301	2.5	2.2
OSWI-3000 hrs (2)	296	2.7	1.9

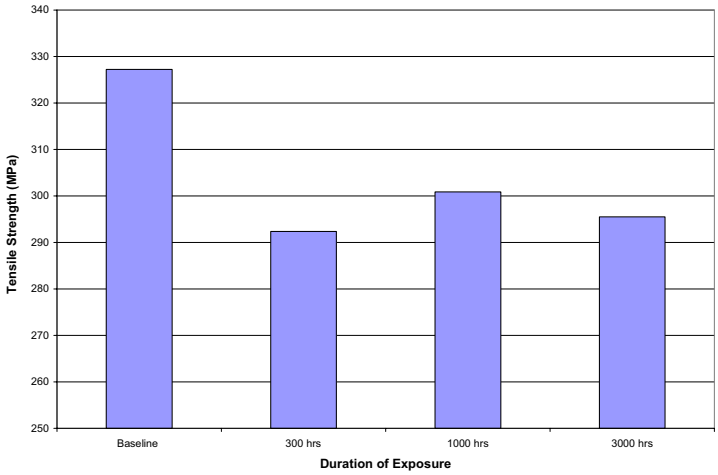

Figure 4.15: Effect of exposure time on the tensile strength of GFRE composite for Oxygen-Saltwater condition

4.2 Fatigue Test Results

The results for GFRV1, GFRV2 and GFRE pipes are presented as the S-N Curves generated from the fatigue testing program as described in chapter 3. All three materials show an alarmingly very poor fatigue resistance. Extrapolation of the fatigue data would indicate that at 10^6 cycles, the fatigue strength of GFRV1, GFRV2, and GFRE materials would be 5 MPa, 20 MPa, and 25 MPa, respectively. These values when compared with their respective tensile strengths of 253 MPa, 202 MPa, and 322 MPa, reveal that their respective fatigue strengths (at 10^6 cycles) for the GFRV1, GFRV2, and GFRE materials occur at as low as only 2 %, 10 % and 8 % of their tensile strengths. These extremely low values of fatigue strengths for these three materials should be a matter of serious concern in their applications where cyclic loading is a critical component of the service conditions. The results are presented and discussed as under:

4.2.1 Outdoor Exposures

The fatigue test results for the GFRV1 material exposed to natural outdoor environment in Dhahran region for a period of 3,6 and 12 months were shown in Figure 4.16. The results show that the natural outdoor exposure for a

Table 4.9: Fatigue data for GFRV1 baseline

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.5	54.5	1200
40%	7.6	43.5	4909
30%	5.7	32.7	19,261
30%	5.7	32.7	21,021
20%	3.8	21.8	109,528

period of 3 months resulted in an improvement in fatigue resistance of the GFRV1 material. The fatigue strength increased from 22 MPa to 27 MPa at 10^5 cycles. The fatigue life enhancement by a factor of about 2.5 is noted after 3 months of exposure.

This improvement in the fatigue resistance is however lowered after 6 months of outdoor exposure. However, the fatigue strength of the GFRV1 material even after 12 months remained higher than the fatigue strength of the as received (un-exposed) material. These results suggest that the environmental conditions begin to induce their detrimental effects on the material after the initial beneficial effect that could be attributed to curing during the initial 3 months exposure (Figure 4.20).

Examination of the fractured specimens by scanning electron microscope revealed degradation of the material. The fracture surfaces of the 12 month natural outdoor exposed samples show clear matrix embrittlement which has

Table 4.10: Fatigue data for GFRV1 Composite for 3 months natural exposure

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	8.8	54.5	2604
50%	8.6	54.5	3909
40%	7.4	43.6	7189
30%	5.5	32.7	32,562
30%	5.4	32.7	37,320
20%	3.9	21.8	254,998

Table 4.11: Fatigue data for GFRV1 for 6 months natural exposure

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	8.9	54.5	3061
40%	7.5	54.5	5043
40%	8.4	43.6	7032
30%	6.0	32.7	17,874
30%	6.1	32.7	20,224
20%	3.3	21.8	145,559

Table 4.12: Fatigue data for GFRV1 for 12 months natural exposure

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.0	54.5	2346
40%	7.8	54.5	5573
40%	8.0	43.6	5964
30%	5.8	32.7	25,803
30%	5.1	32.7	26,635
20%	3.6	21.8	155,178

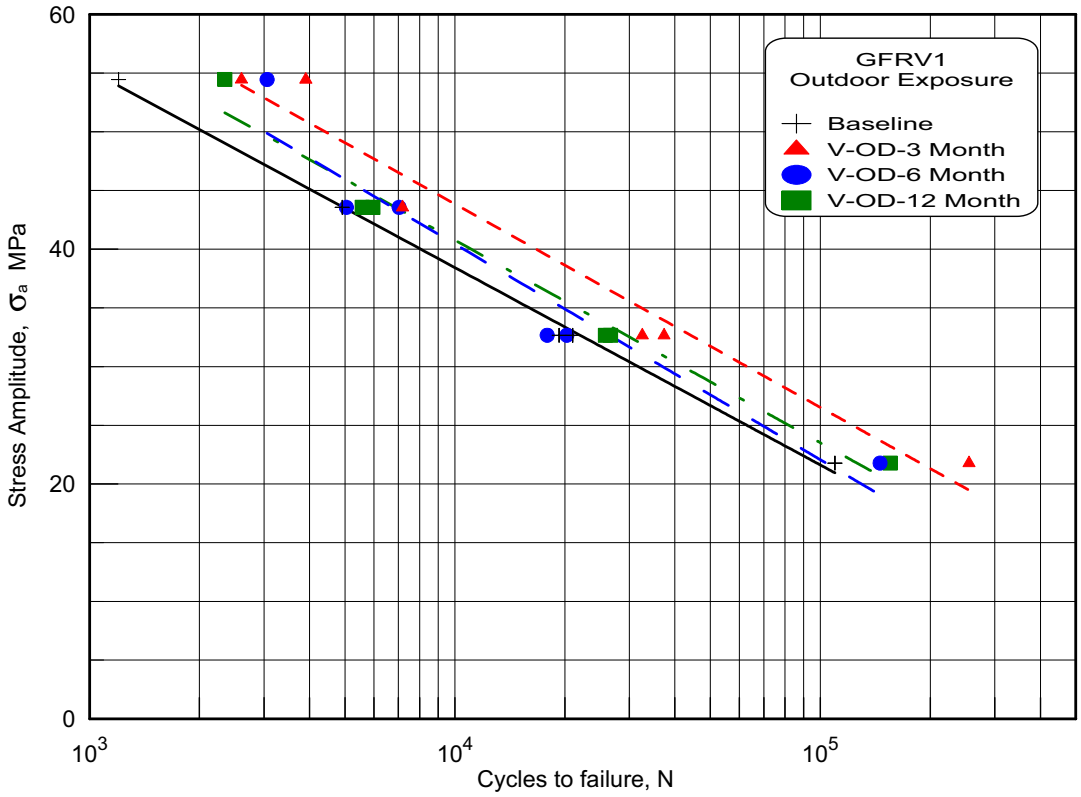

Figure 4.16: S-N curve for GFRV1 pipe material exposed to outdoor exposure condition

Table 4.13: Fatigue data for GFRV1 for a 6 month oil filled natural exposure

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.2	54.5	2320
40%	7.3	43.6	5043
40%	7.3	43.6	7032
30%	5.6	32.7	17,874
30%	5.3	32.7	20,224
20%	3.7	21.8	145,559

resulted in matrix cracks. The brittle fracture of the fiber can also be clearly seen in Figure 4.18. The fractured specimen also shows fiber fracture in GFRV1 pipes for 12 months exposure (Figure 4.19).

Outdoor Exposure of Crude Oil filled pipes

Exposure of pipes filled with crude oil to out door natural environment for a period of 6 months shows a slight improvement in the fatigue resistance in the low cycle region and a slight reduction in the high cycle region. After 12 months of exposure, the oil filled pipes showed a further improvement in the fatigue resistance of the composite in the low cycle region. A fatigue life enhancement by a factor of 2.5 was observed for 12 month exposure (Figure 4.20).

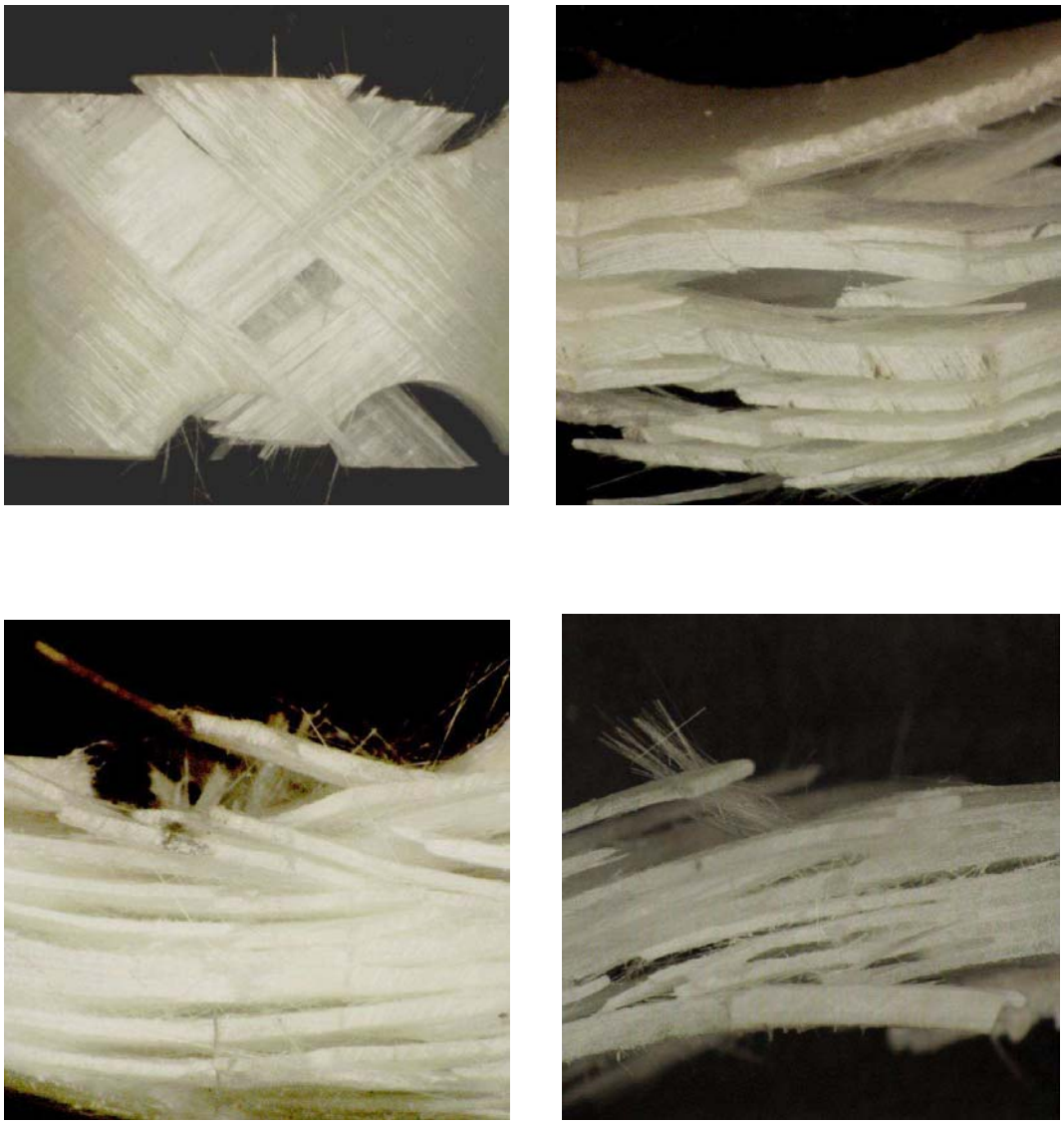

Figure 4.17: Optical micrographs showing the fatigue fracture in as received GFRV2 pipe material

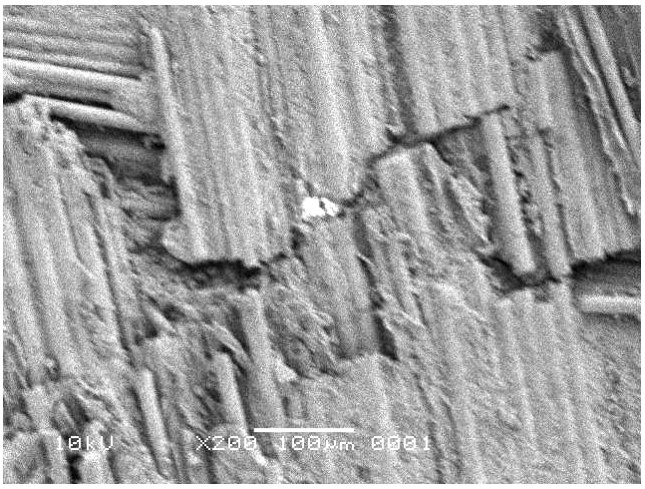

Figure 4.18: SEM microscopic image depicting matrix embrittlement for GFRV1 pipe material exposed to natural outdoor condition for 12 months

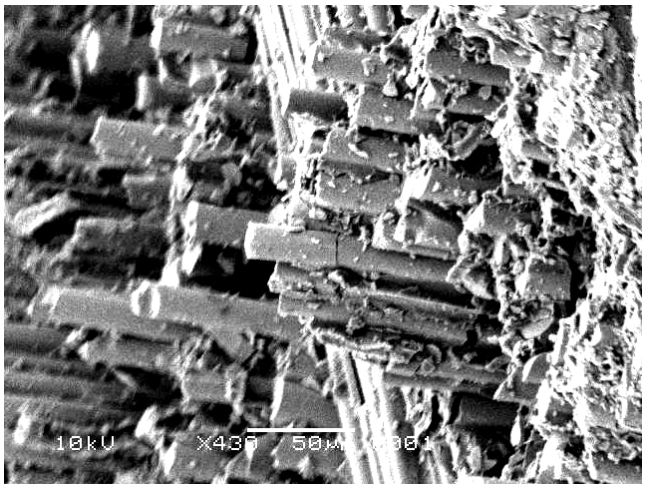

Figure 4.19: SEM microscopic image depicting fiber fracture for GFRV1 pipe material exposed to natural outdoor condition for 12 months

Table 4.14: Fatigue data for GFRV1 for a 12 month oil filled natural exposure

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.3	54.5	2836
40%	8.5	43.6	6235
40%	7.8	43.6	7567
30%	6.1	32.7	26,838
30%	6.4	32.7	21,829
20%	3.6	21.8	75,111

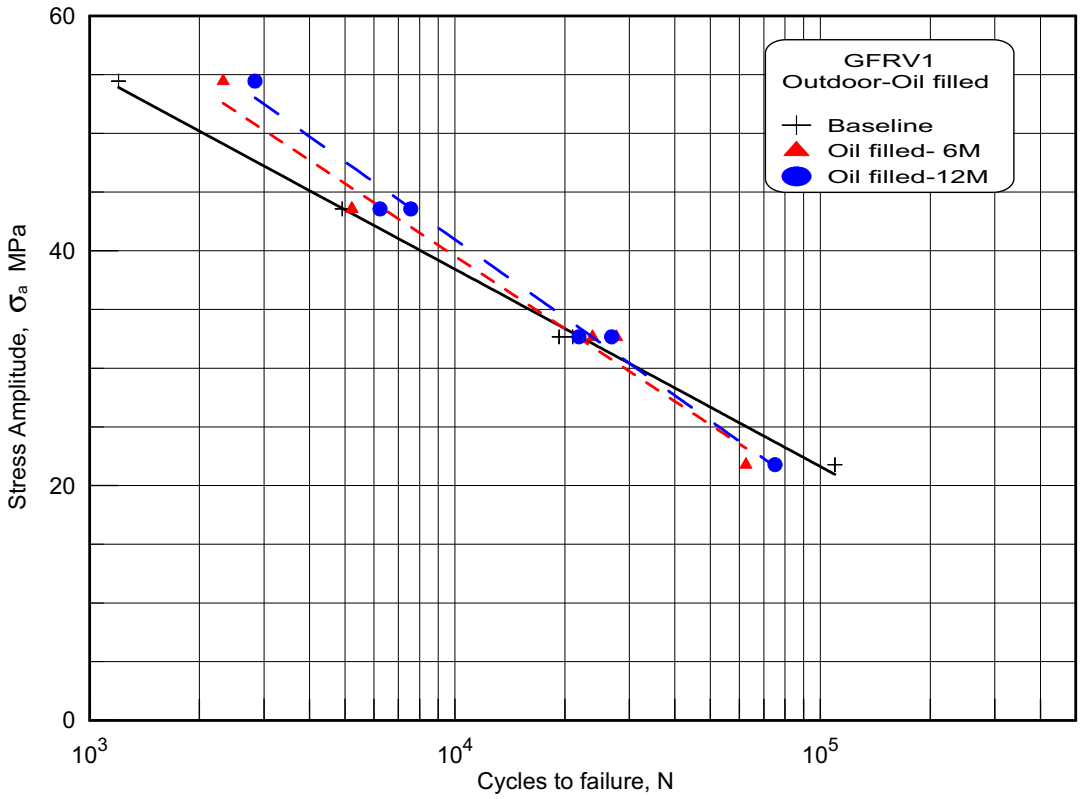

Figure 4.20: S-N curve for GFRV2 pipe material exposed to oil filled outdoor exposure condition

Table 4.15: Fatigue data for GFRV1 for 12 month sea water immersion

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.4	54.5	1834
40%	7.7	43.6	6224
30%	5.9	32.7	18,577
30%	6.2	32.7	15,486
20%	3.8	21.8	152,953

Sea Water Immersion

The fatigue test results for GFRV1 pipes exposed to gulf sea water are provided in Figure 4.21. As can be seen from the above S-N curve that the 12-month immersion in gulf sea water resulted in no degradation; rather a slight improvement in the fatigue resistance of the pipe was observed.

4.2.2 Accelerated Exposures

The fatigue test results values for the GFRV2 Base line are shown in Table 4.16. The specimens have relatively high fiber content, which may affect the quality of interface between the fibers and the matrix. For this reason, poor bonding may result at the interface between the matrix and the fiber. There was a clear evidence of poor adhesion between the fiber and the matrix in (Figure 4.23). Accordingly, fiber pullout and layer delamination are identi-

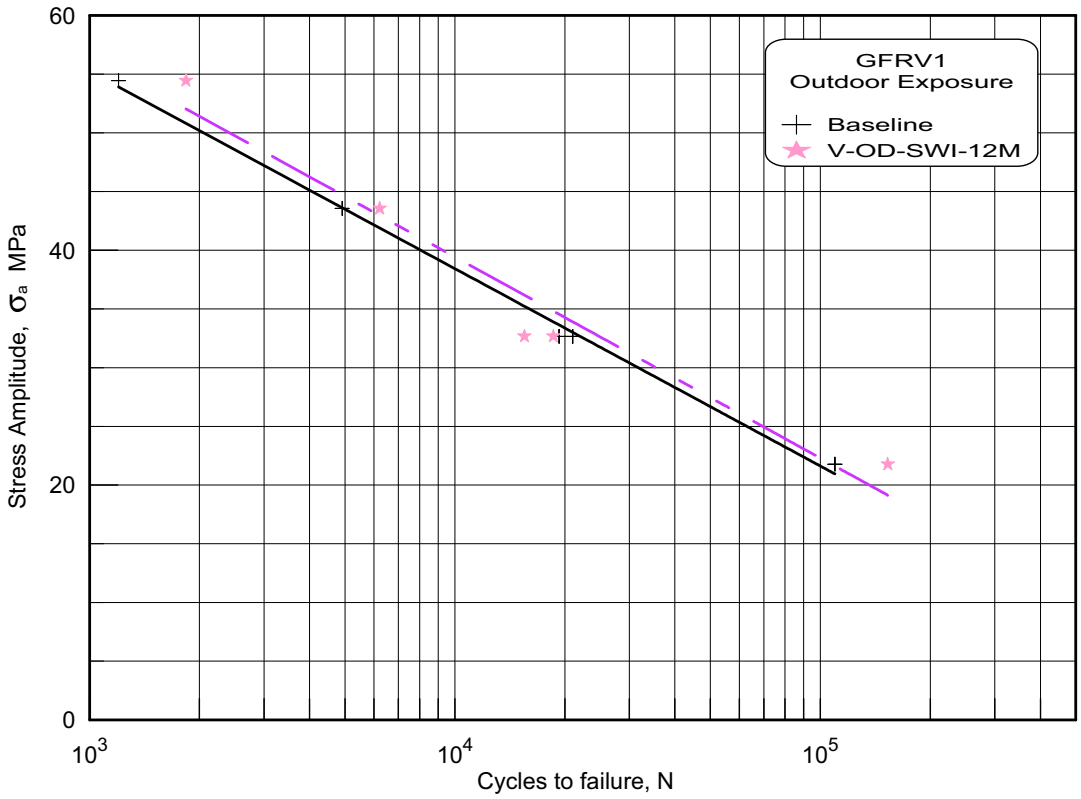

Figure 4.21: S-N curve for GFRV2 pipe material exposed to sea water filled exposure condition

Table 4.16: Fatigue data for GFRV2 Baseline

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.1	54.5	1830
50%	10.0	54.5	2824
50%	10.3	54.5	2822
40%	7.7	43.6	12,128
40%	8.0	43.6	7446
30%	6.1	32.7	97,869
30%	5.8	32.7	179,525
30%	6.5	32.7	67,125
20%	3.9	21.8	2,000,000

fied as predominant failure mechanisms. Helical cracks were also visible on the fiber surface (Figure 4.25) which indicate fiber rupture taking place in the composite. There was also evidence of fiber matrix debonding on the fractured surface (Figure 4.22).

Dry heat Exposure

Figure 4.26 shows the S-N curves for GFRV2 specimens exposed to dry heat condition at 40^0C. This dry heat temperature of 40^0C did not produce any noticeable change in the fatigue strength of GFRV2 for the durations of 300, 1000 and 3000 hours, rather a slight decrease in the fatigue resistance was noted at high stress values. However, as the exposure period is extended to 10,000 hours, a slight degradation was observed with fatigue life decreasing

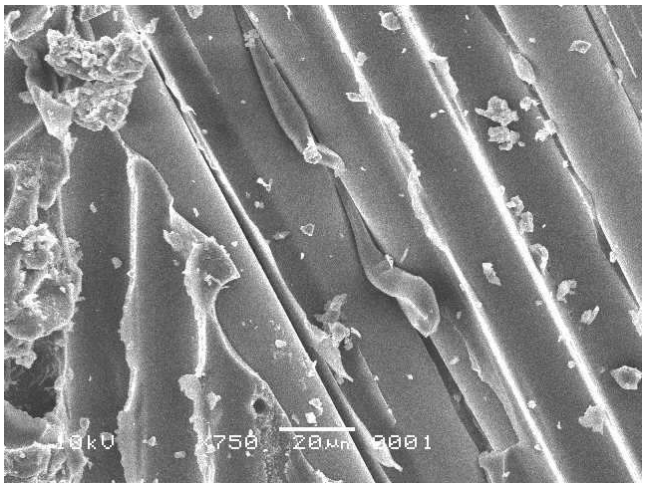

Figure 4.22: SEM microscopic image showing debonding at fiber-matrix interface for the as received GFRV2 pipe material

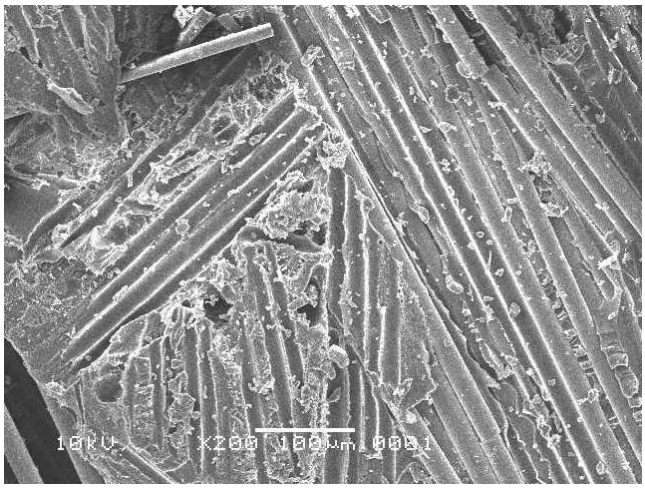

Figure 4.23: SEM microscopic image showing poor adhesion between fiber and the resin for the as received GFRV2 pipe material

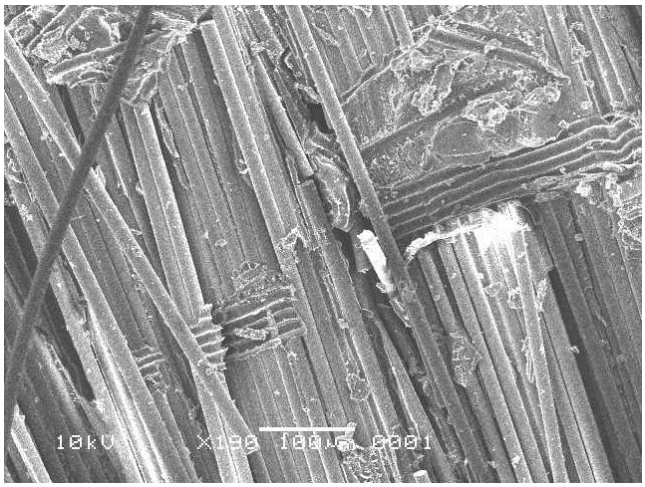

Figure 4.24: SEM microscopic image showing complete separation at interface between fiber and matrix for the as received GFRV2 pipe material

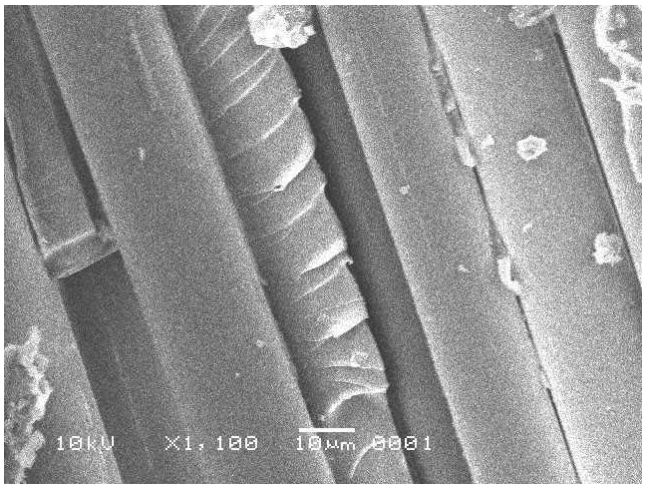

Figure 4.25: SEM microscopic image showing helical crack on the fiber surface for the as received GFRV2 pipe material

Table 4.17: Fatigue data for GFRV2 composite for Dry heat-40^0C exposed for 300 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.9	54.5	2774
50%	9.5	54.5	6721
40%	7.5	43.6	4761
40%	7.9	43.6	7694
30%	5.8	32.7	56,452
30%	5.6	32.7	88,464
20%	3.8	21.8	727,255

Table 4.18: Fatigue data for GFRV2 composite for Dry heat-40^0C exposed for 1000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.3	54.5	2840
50%	9.6	54.5	1802
40%	7.6	43.6	13,058
30%	5.9	32.7	63,056
30%	5.6	32.7	57,895
20%	3.8	21.8	1,101,713

by a factor of 4 and the fatigue strength decreasing by 3 MPa at low cycle regions.

A further increase of dry heat temperature for 70^0C produces a noticeable effect with fatigue life improving by a factor of 4 in low cycle and high stress regions for 300 hours (Figure 4.27).

In fact at 1000 hours of exposure at 70^0C, the fatigue strength seems to get further enhanced as compared to 300 hours of exposure. Figure 4.27

Table 4.19: Fatigue data for GFRV2 composite for Dry heat-40^0C exposed for 3000 hrs

% of tensile strength	**P amp (KN)**	**Stress amplitude (MPa)**	**Life(cycles)**
50%	9.0	54.5	2377
40%	7.8	43.6	13,745
40%	8.2	43.6	10,504
30%	6.0	32.7	92,602
30%	5.9	32.7	115,122
20%	3.9	21.8	2,000,000

Table 4.20: Fatigue data for GFRV2 composite for Dry heat-40^0C exposed for 10,000 hrs

% of tensile strength	**P amp (KN)**	**Stress amplitude (MPa)**	**Life(cycles)**
50%	10.5	54.5	1830
40%	8.1	43.6	6467
40%	7.9	43.6	7728
30%	5.8	32.7	45,464
30%	5.9	32.7	48,766
20%	4.1	21.8	1,078,611

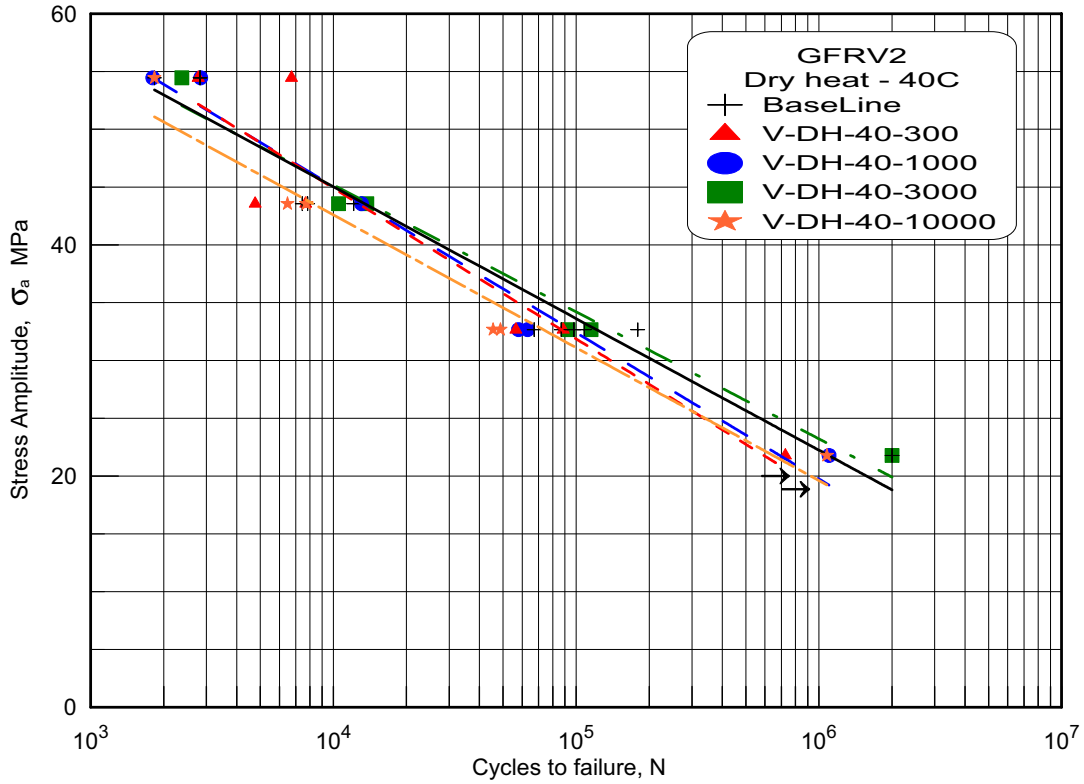

Figure 4.26: S-N curve for GFRV2 pipe material exposed to Dry heat-40^{0}C Condition

Table 4.21: Fatigue values of GFRV2 composite for Dry heat-70^0C exposed for 300 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.0	54.5	2377
40%	7.6	43.6	17,402
40%	8.1	43.6	13,970
30%	5.7	32.7	71,876
30%	5.6	32.7	94,151
20%	3.9	21.8	2,000,000

highlights the effect of exposure time and temperature on the fatigue resistance of GFRV2. This initial increase in the fatigue strength for low exposure periods of 300 hours can be explained by the curing process which is more predominant initially at higher temperatures.

Even 10,000 hours of exposure did not result in any degradation of the material, in fact it enhanced the fatigue strength by almost 5 MPa at 10^4 cycles. The fatigue life improved by 7 orders at high stress regions. This improvement in the fatigue strength at low cycle regions was consistent at higher exposure periods.

UV Exposure

For the specimens exposed for 100 hours in UV condition, no significant change in the fatigue resistance and fatigue life of the composite was observed

Table 4.22: Fatigue data for GFRV2 composite for Dry heat-70^{0}C exposed for 1000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.5	54.5	7462
40%	7.4	43.6	19,552
40%	7.4	43.6	20,550
30%	5.6	32.7	132,416
30%	5.5	32.7	89,614
20%	4.1	21.8	2,000,000

Table 4.23: Fatigue data for GFRV2 composite for Dry heat-70^{0}C exposed for 3000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.1	54.5	2347
40%	7.7	43.6	16,768
40%	8.0	43.6	6736
30%	5.8	32.7	81,794
30%	5.9	32.7	65,927
20%	4.0	21.8	1,054,604

Table 4.24: Fatigue data for GFRV2 composite for Dry heat-70^{0}C exposed for 10,000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.2	54.5	4932
40%	7.3	43.6	22,033
40%	7.6	43.6	51,658
30%	5.9	32.7	127,239
30%	5.5	32.7	191,326
20%	4	21.8	1,017,781

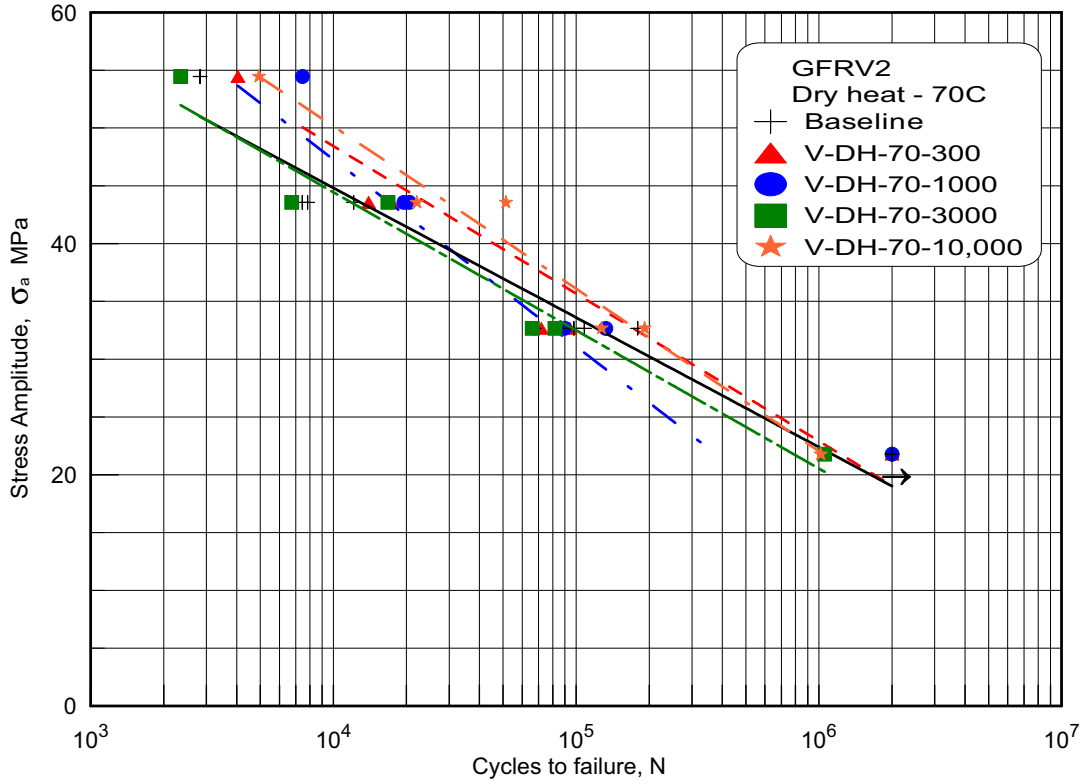

Figure 4.27: S-N curve for GFRV2 pipe material exposed to Dry heat-70^{0}C Condition

Table 4.25: Fatigue data for GFRV2 composite exposed to UV radiation for 100 hrs

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10	54.5	2610
40%	7.6	43.6	12,361
30%	5.8	32.7	48,081
30%	6.1	32.7	89,709
20%	3.9	21.8	796,031

Figure 4.28: Optical micrographs showing fatigue fracture for GFRV2 pipe material exposed to Dry heat-70^{0}C condition for 1000 hours

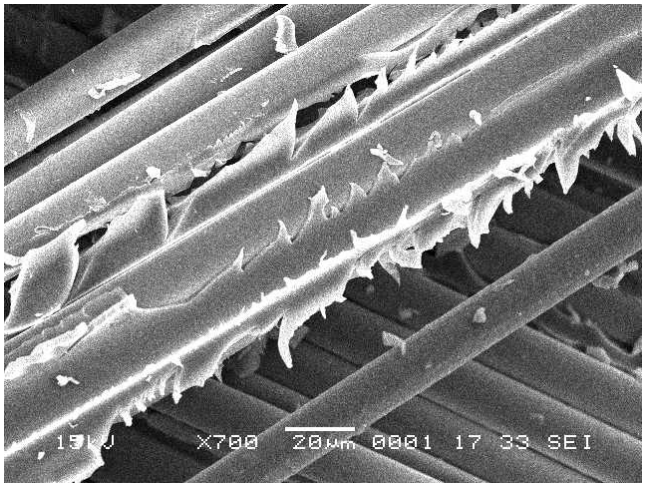

Figure 4.29: SEM microscopic image depicting brittle behavior of matrix for GFRV2 pipe material exposed to Dry heat-70^{0}C condition for 1000 hours

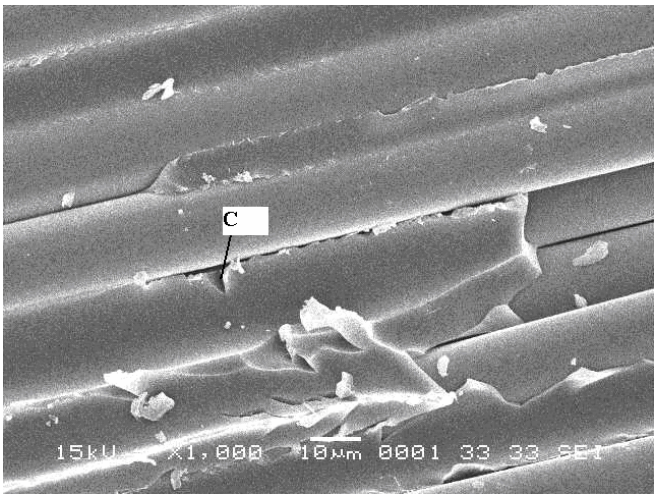

Figure 4.30: SEM microscopic image depicting matrix crack for GFRV2 pipe material exposed to Dry heat-70^0C condition for 1000 hours

Table 4.26: Fatigue data for GFRV2 composite exposed to UV radiation for 300 hrs

% of tensile strength	**P amp (KN)**	**Stress amplitude (MPa)**	**Life(cycles)**
50%	10	54.5	643
40%	8	43.6	5478
40%	7.8	43.6	9621
30%	5.9	32.7	49,687
30%	5.9	32.7	34,850
20%	3.8	21.8	2,000,000

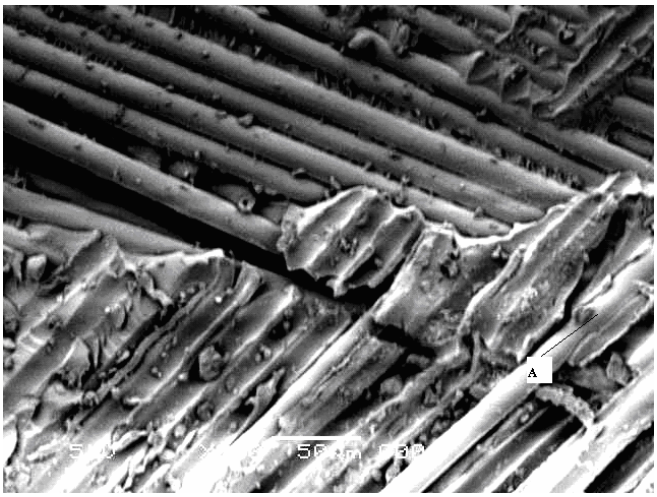

Figure 4.31: SEM microscopic image showing good resin adhesion to the fiber for GFRV2 pipe material exposed to Dry heat-70^{0}C condition for 3000 hours

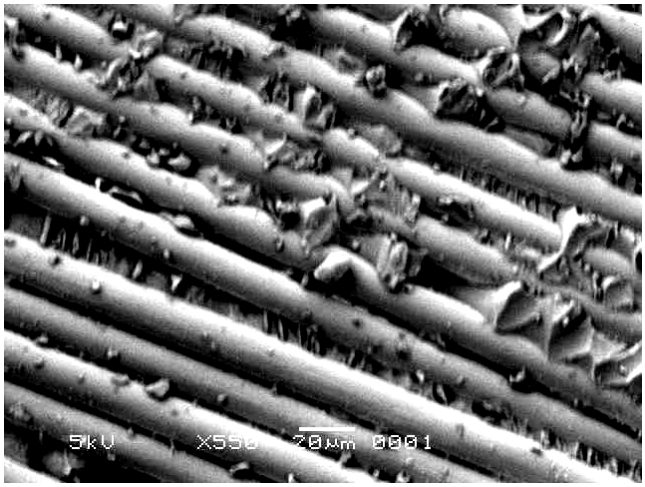

Figure 4.32: SEM microscopic image depicting matrix plasticization for GFRV2 pipe material exposed to Dry heat-70^{0}C condition for 3000 hours

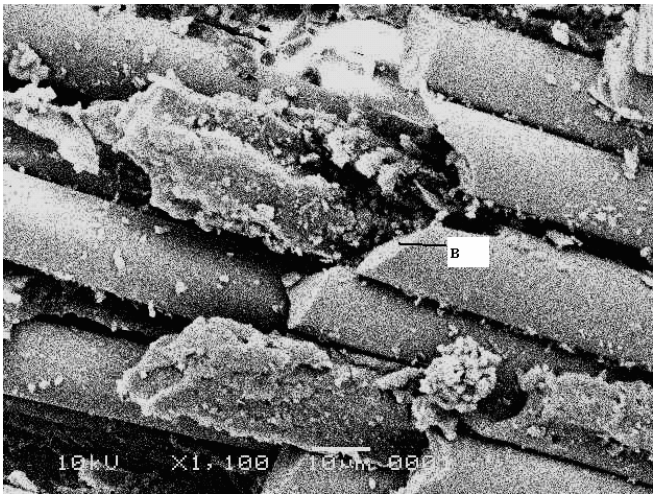

Figure 4.33: SEM microscopic image showing shear fracture of fibers for GFRV2 pipe material exposed to Dry heat-70^{0}C condition for 3000 hours

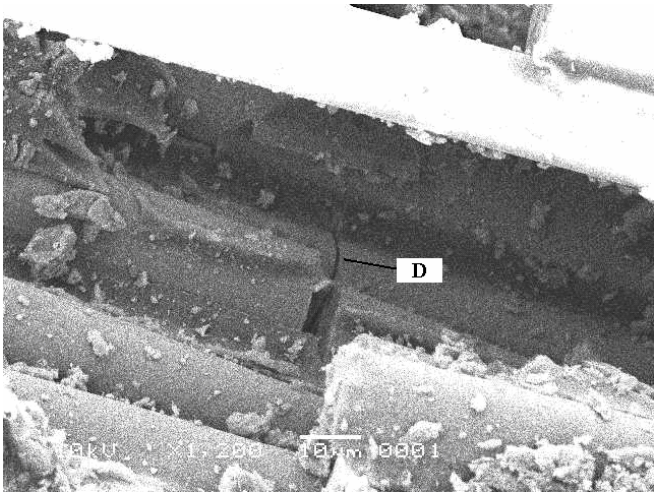

Figure 4.34: SEM microscopic image showing fiber fracture for GFRV2 pipe material exposed to Dry heat-70^{0}C condition for 3000 hours

Table 4.27: Fatigue data for GFRV2 composite exposed to UV radiation for 1000 hrs

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10	54.5	813
40%	7.9	43.6	5491
40%	7.8	43.6	11,124
30%	6	32.7	93,374
30%	5.6	32.7	112,322
20%	4.1	21.8	522,570

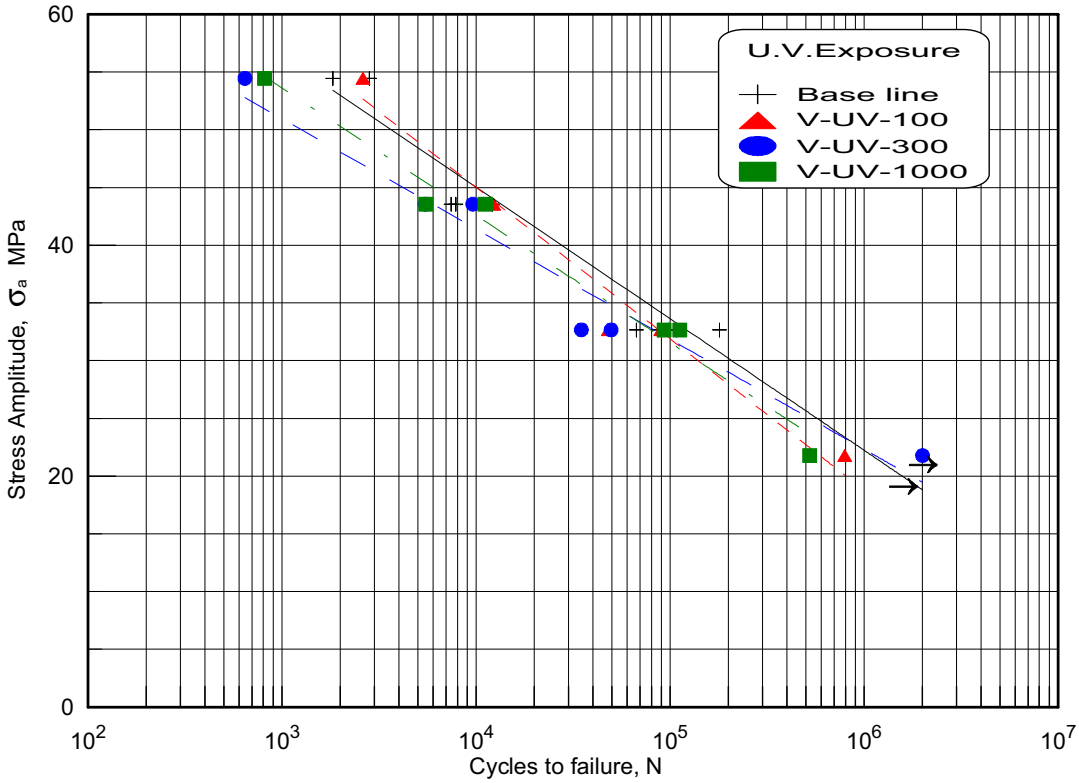

Figure 4.35: S-N curve for GFRV2 pipe material exposed to UV radiation

(Figure 4.35). However, its effect is clearly seen as the exposure period reaches 300 hours. The fatigue strength decreased by about 6 MPa at 2×10^3 cycles of failure and fatigue life by a factor of 3 at 50 MPa. Such considerable degradation was not observed for other temperature based exposures even at higher exposure periods (such as dry heat 40^0C at 10,000 hours of exposure). This highlights the significance of UV radiation on the durability of the GFRV2 composite.

Humidity Exposure

No clear trend of enhancement or degradation of fatigue resistance was observed when GFRV2 was exposed to ambient humidity condition (Figure 4.37) up to 10,000 hours of exposure. However for the 100% RH condition, a slight degradation in fatigue strength was observed at higher exposure period of 10,000 hours. The fatigue strength and the fatigue life reduced by about 2 MPa and 2 orders respectively at low cycle regions.

Table 4.28: Fatigue data for GFRV2 composite for 100% Humidity exposed for 300 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.6	54.5	2286
40%	8	43.6	10,139
40%	8	43.6	13,077
30%	5.9	32.7	107,186
30%	5.9	32.7	115,390
20%	4.1	21.8	1,348,551

Table 4.29: Fatigue data for GFRV2 composite for 100% Humidity exposed for 1000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.6	54.5	2335
40%	7.7	43.6	15,205
40%	8	43.6	14,668
30%	5.9	32.7	121,979
30%	5.9	32.7	91,076
20%	3.9	21.8	2,000,000

Salt Spray Exposure

The effect of salt water spray on the fatigue resistance of GFRV2 is shown in Figure 4.38. Exposure to salt spray (at room temperature) for 300 hours of exposure produced a clear trend of reduction in the fatigue strength. This reduction becomes more apparent at the initial exposure periods. However, with further increase in the exposure period, this degradation in the fatigue resistance was compensated. The fatigue life which was reduced by 2 orders

Table 4.30: Fatigue data for GFRV2 composite for 100% Humidity exposed for 3000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	10.1	54.5	1575
40%	8.1	43.6	7981
40%	7.6	43.6	8298
30%	6	32.7	131,291
30%	5.7	32.7	159,191
20%	3.7	21.8	2,000,000

Table 4.31: Fatigue data for GFRV2 composite for 100% Humidity exposed for 10,000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.9	54.5	1848
40%	7.8	43.6	6876
40%	7.8	43.6	5011
30%	6	32.7	173,057
30%	6	32.7	127,188
20%	3.7	21.8	2,000,000

Table 4.32: Fatigue data for GFRV2 composite for Ambient Humidity exposed for 1000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.8	54.5	2777
40%	7.6	43.6	17,965
40%	7.8	43.6	13,333
30%	5.9	32.7	101,124
30%	5.8	32.7	113,518
20%	3.7	21.8	2,000,000

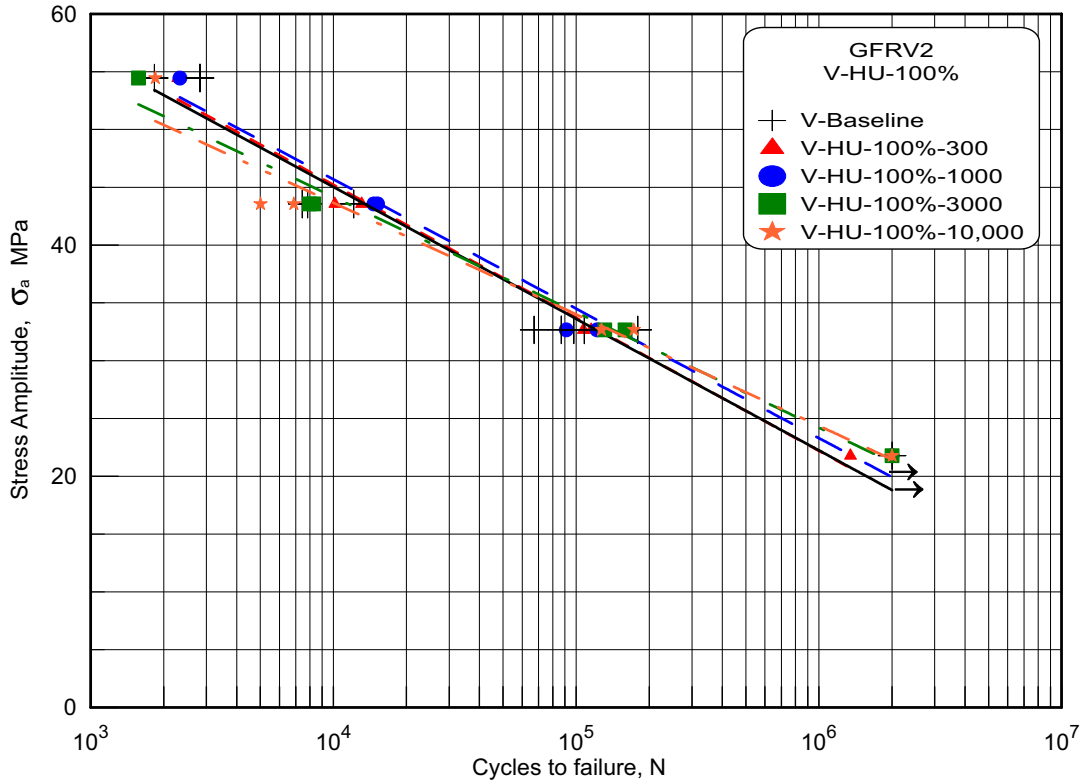

Figure 4.36: S-N curve for GFRV2 pipe material exposed to 100% Humidity condition

Table 4.33: Fatigue data for GFRV2 composite for Ambient Humidity exposed for 3000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.8	54.5	2847
40%	7.7	43.6	6160
40%	8	43.6	6228
30%	5.6	32.7	66,083
30%	5.8	32.7	178,423
20%	4.0	21.8	2,000,000

Table 4.34: Fatigue data for GFRV2 composite for Ambient Humidity exposed for 10,000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.8	54.5	3260
40%	8	43.6	11,500
40%	7.9	43.6	7980
30%	6.1	32.7	97,659
30%	6	32.7	100,469
20%	4.1	21.8	2,000,000

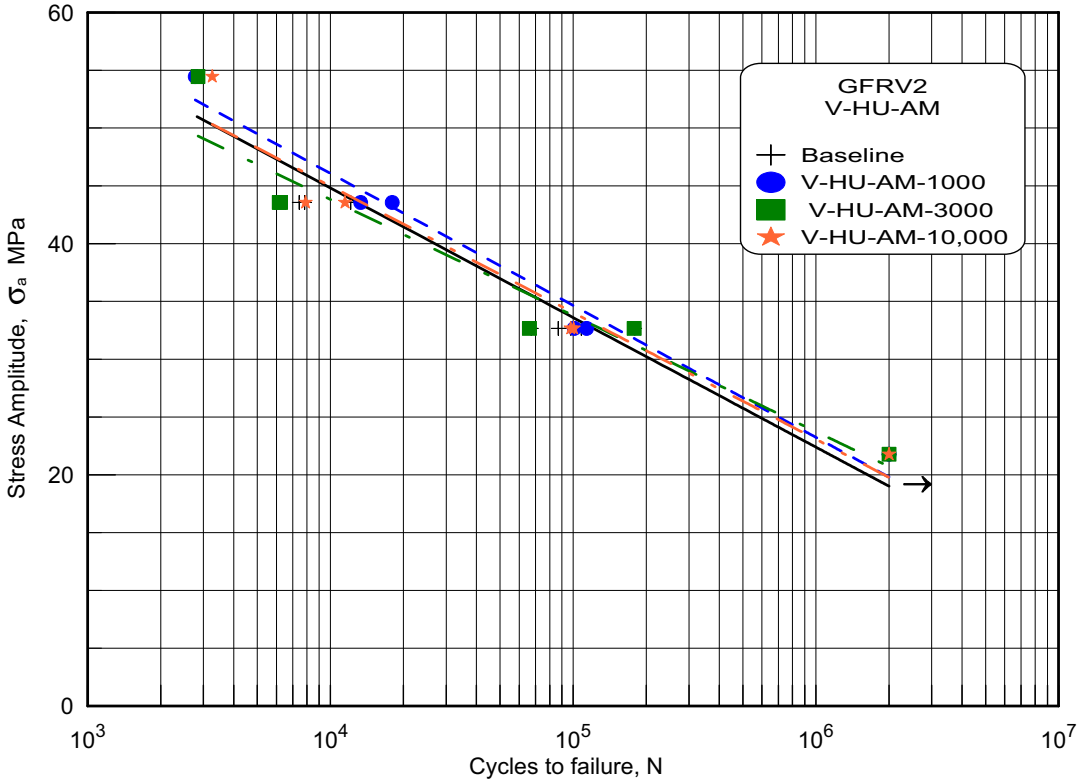

Figure 4.37: S-N curve for GFRV2 pipe material exposed to ambient humidity condition

Table 4.35: Fatigue data for GFRV2 composite for Saltwater spray exposed for 300 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.4	54.5	1848
40%	7.6	43.6	9831
40%	7.5	43.6	7177
30%	5.9	32.7	31,790
30%	5.9	32.7	78,878
20%	4	21.8	2,000,000

Table 4.36: Fatigue data for GFRV2 composite for Saltwater spray exposed for 1000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.3	54.5	2362
40%	7.3	43.6	7659
40%	7.3	43.6	13,826
30%	5.5	32.7	69,032
30%	5.7	32.7	94,207
20%	3.8	21.8	8,66,567

of magnitude for 300 hours of exposure was later compensated. A plausible explanation can be made that longer exposure periods of 10,000 hours did not produce any noticeable change in the fatigue resistance of the GFRV2 composite.

Table 4.37: Fatigue data for GFRV2 composite for Saltwater spray exposed for 3000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.8	54.5	1871
40%	7.9	43.6	6892
40%	7.3	43.6	8417
30%	5.7	32.7	89,912
30%	5.5	32.7	158,416
20%	3.7	21.8	902,657

Table 4.38: Fatigue data for GFRV2 composite for Saltwater spray exposed for 10,000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.4	54.5	1862
40%	7.5	43.6	8022
40%	7.9	43.6	5729
30%	5.5	32.7	76,641
30%	5.5	32.7	177,182
20%	3.7	21.8	1,809,965

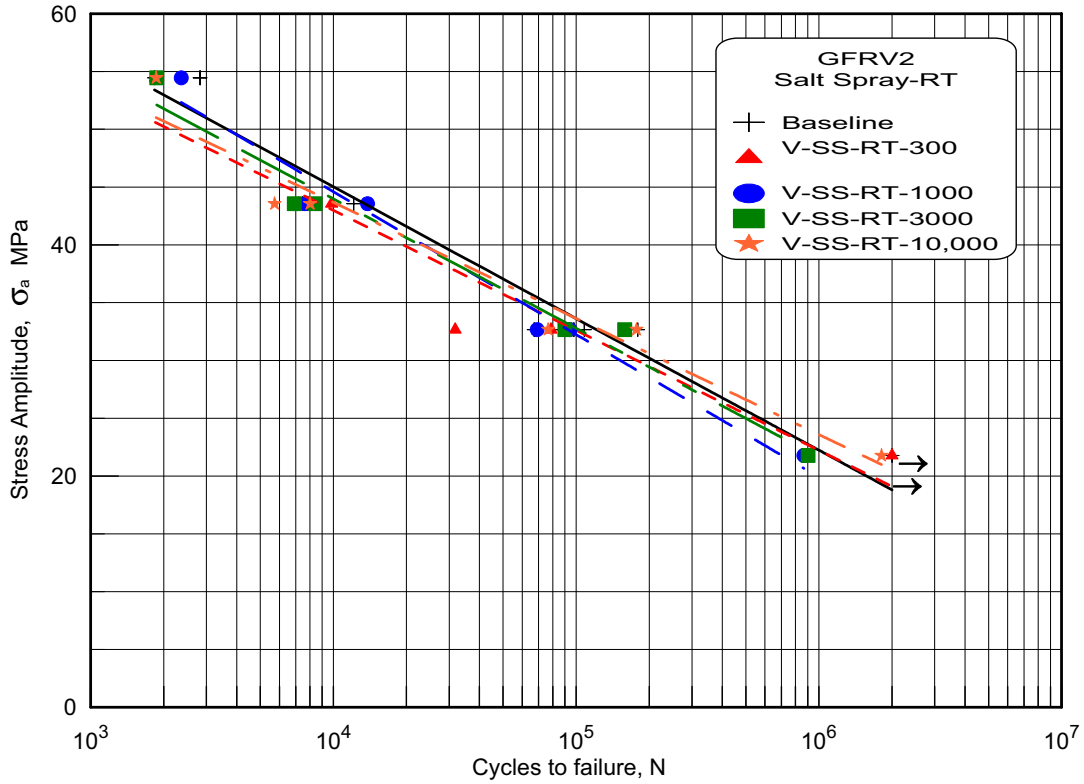

Figure 4.38: S-N curve for GFRV2 pipe material exposed to Salt Spray Condition

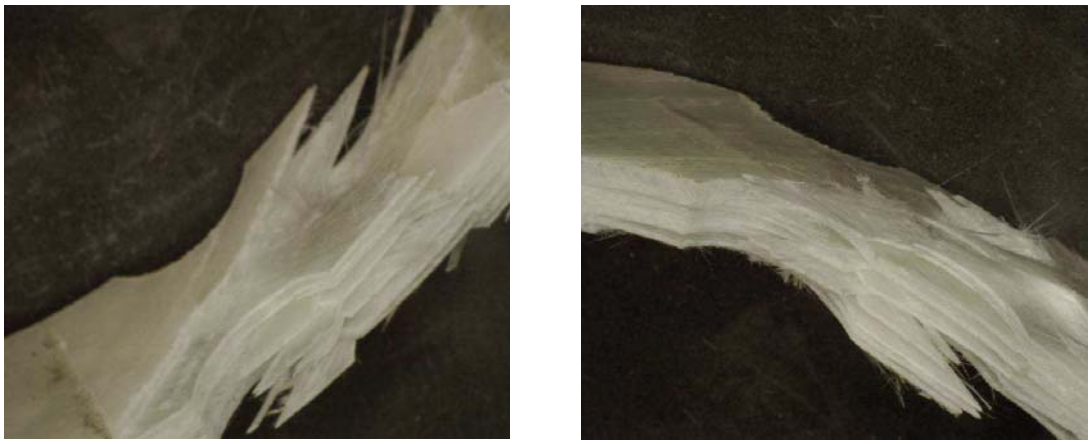

Figure 4.39: Optical microscopic images for Salt Spray condition exposed for 3000 hours

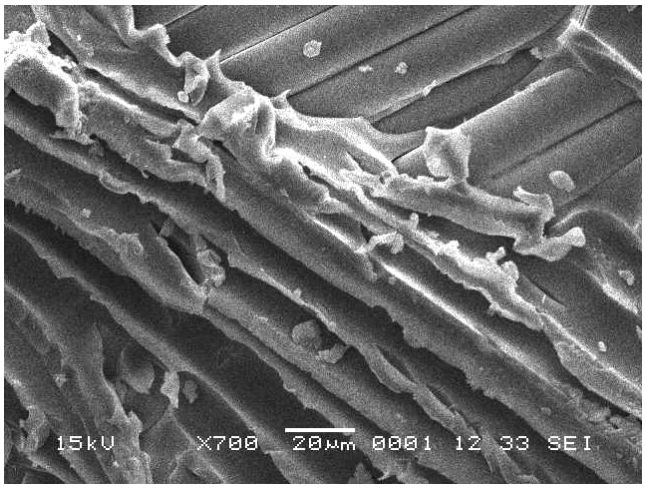

Figure 4.40: SEM microscopic image depicting brittle failure of the matrix for GFRV2 pipe material exposed to Salt Spray condition for 3000 hours

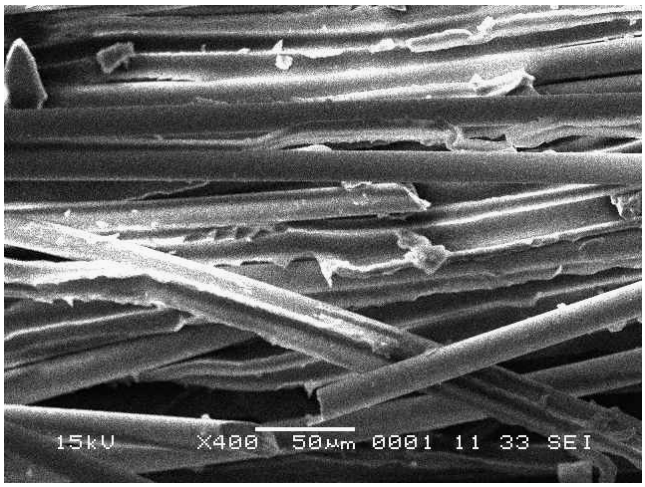

Figure 4.41: SEM microscopic image in which plasticization is not visible for GFRV2 pipe material exposed to Salt Spray condition for 3000 hours

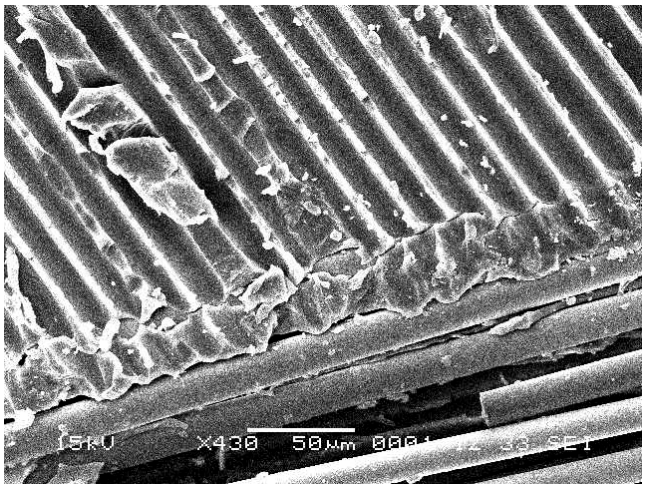

Figure 4.42: SEM microscopic image depicting fiber devoid of resin for GFRV2 pipe material exposed to Salt Spray condition for 3000 hours

Table 4.39: Fatigue data for GFRV2 composite for Oxygen-saltwater immersion exposed for 300 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.7	54.5	1206
40%	7.7	43.6	8566
40%	7.7	43.6	13,303
30%	5.8	32.7	90,487
30%	5.9	32.7	101,732
20%	3.8	21.8	858,502

Table 4.40: Fatigue data for GFRV2 composite for Oxygen-saltwater immersion exposed for 1000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	11.6	54.5	826
40%	8.1	43.6	11,077
40%	7.9	43.6	4671
30%	5.7	32.7	116,863
30%	6.0	32.7	60,866
20%	3.9	21.8	1,616,526

Oxygenated salt water immersion

Immersion of GFRV2 in 100% oxygenated seawater resulted in deterioration of fatigue resistance with exposure time (Figure 4.43). This degradation effect was more pronounced in the low cycle region (about 4 MPa reduction at 2×10^3 cycles and fatigue life by 2.5 orders of magnitude for 3000 hours of exposure) and diminished slightly in the high cycle region.

Table 4.41: Fatigue data for GFRV2 composite for Oxygen-saltwater immersion exposed for 3000 hours

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	9.8	54.5	1324
40%	7.7	43.6	4682
40%	8.0	43.6	10,933
30%	5.6	32.7	71,748
30%	5.8	32.7	26,074
20%	4.0	21.8	1,330,270

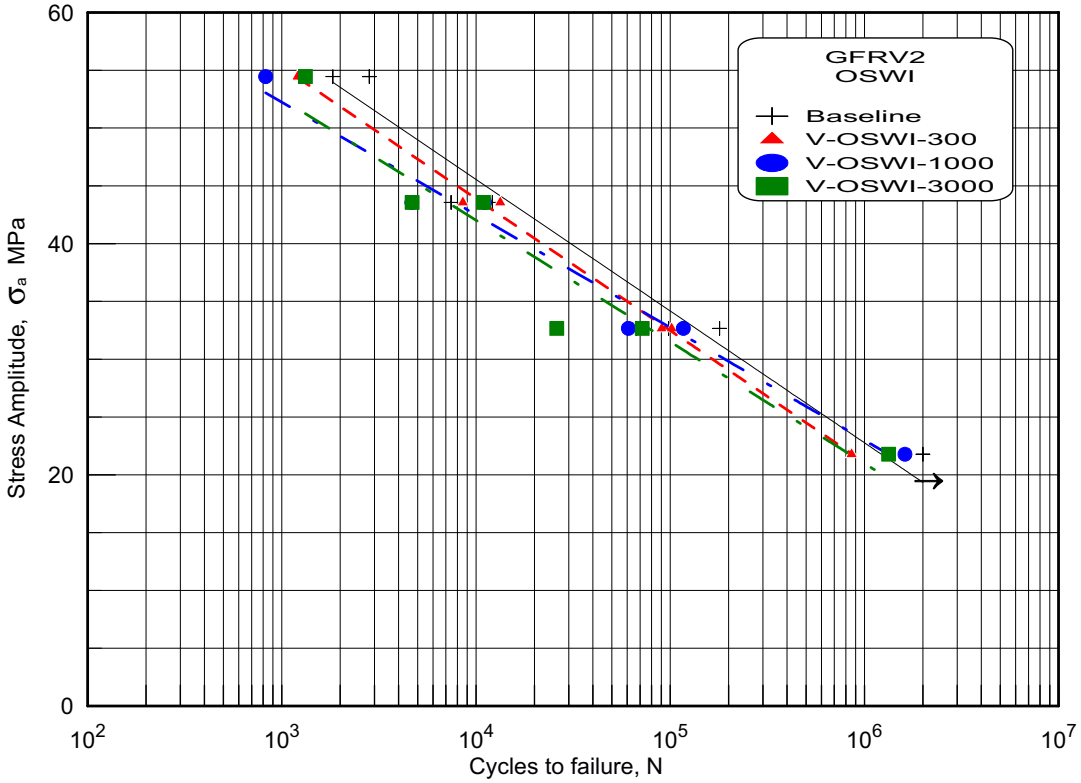

Figure 4.43: S-N curve for the GFRV2 pipe material exposed to OSWI immersion

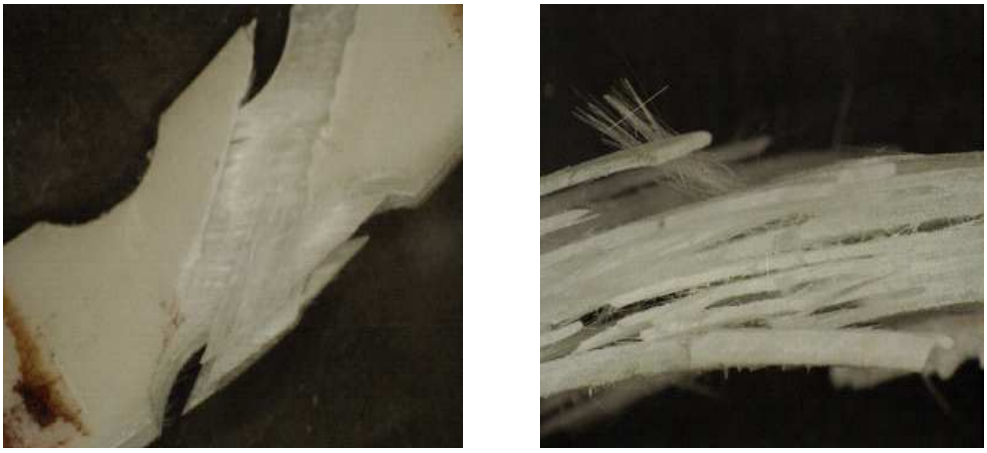

Figure 4.44: Optical micrographs for GFRV2 pipe material exposed to OSWI immersion for 300 hours

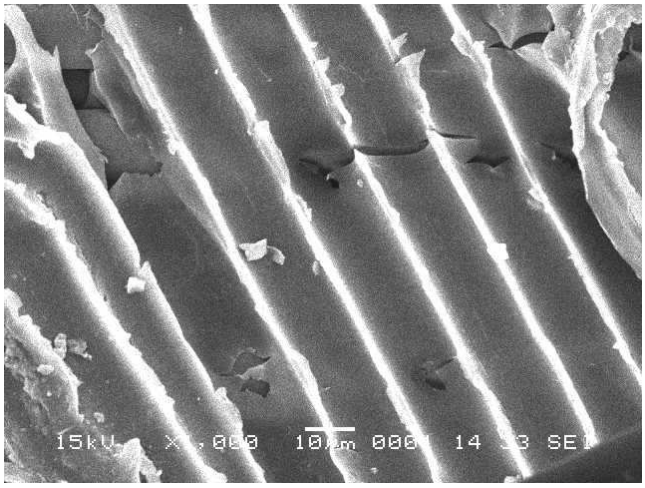

Figure 4.45: SEM microscopic image depicting matrix crack for GFRV2 pipe material exposed to OSWI for 300 hours

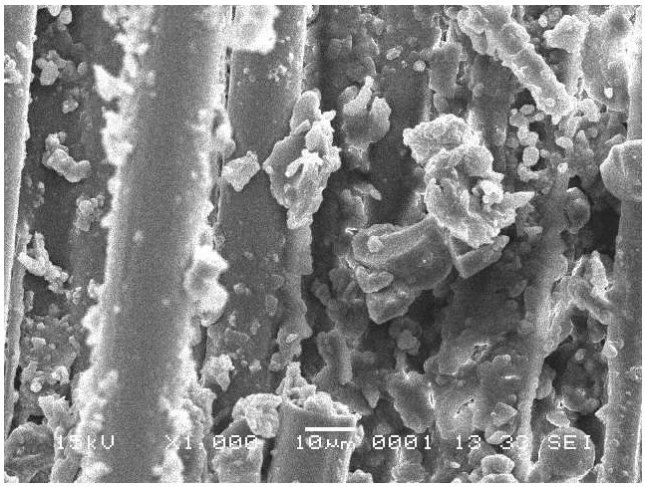

Figure 4.46: SEM microscopic image depicting matrix fragmentation for GFRV2 pipe material exposed to OSWI for 300 hours

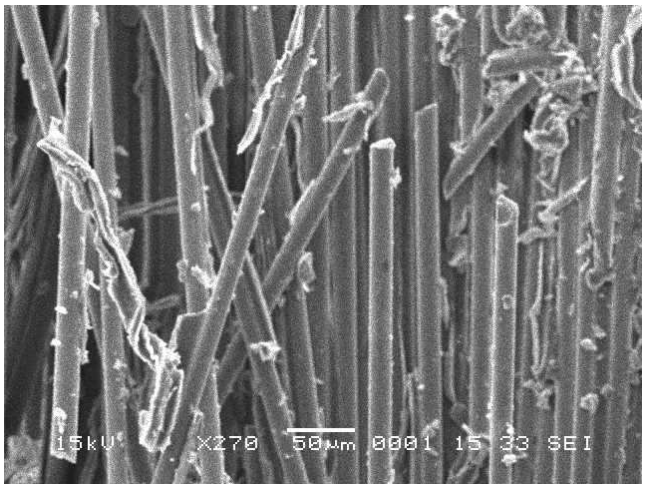

Figure 4.47: SEM microscopic image depicting poor fiber-matrix adhesion for GFRV2 pipe material exposed to OSWI for 300 hours

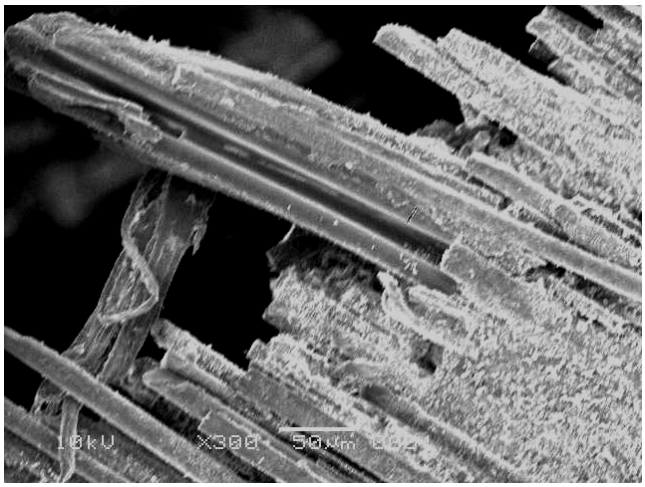

Figure 4.48: SEM microscopic image showing salt debris on the fiber surface for GFRV2 pipe material exposed to OSWI for 3000 hours

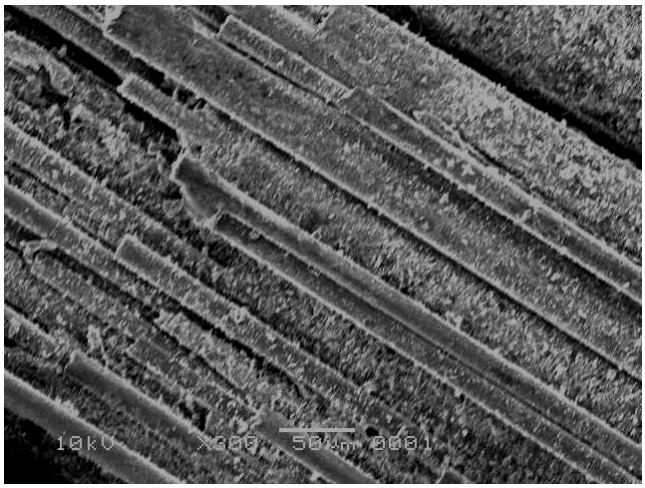

Figure 4.49: SEM microscopic image depicting embrittlement of the fiber for GFRV2 pipe material exposed to OSWI for 3000 hours

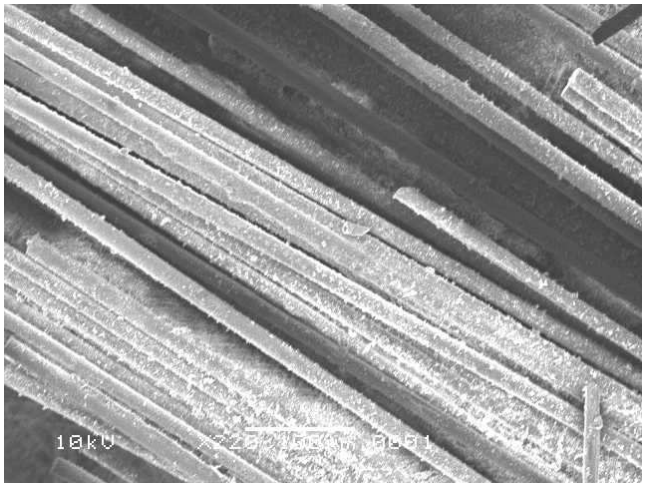

Figure 4.50: SEM microscopic image showing debonding of the fiber-matrix interface for GFRV2 pipe material exposed to OSWI for 3000 hours

4.2.3 GFRE Composite

Fractured surfaces of the epoxy baseline suggest severe fracture occurring for the GFRE composites than the GFRV Composites. Fibers were broken at the fracture surface without being pulled out because of strong matrix-fiber adhesion. Debris due to both matrix and fiber failure was scattered throughout the failure zone and the broken fiber particles from the fiber surface (Figure 4.51) and very poor adhesion between the fiber-matrix interface (Figure 4.52)

The exposure of GFRE to 100% oxygenated saltwater immersion condi-

Table 4.42: Fatigue data for Epoxy baseline tests

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	13.3	73.6	2714
50%	14.6	73.6	1933
40%	11.9	58.9	6554
40%	10.9	58.9	11,954
40%	10.5	58.9	7062
30%	8.1	44.2	32,321
30%	8.3	44.2	50,316
20%	5.2	29.5	537,890
20%	5.5	29.5	635,442

Table 4.43: Epoxy Fatigue data for oxygen saltwater immersion for 300 hrs

% of tensile strength	P amp (KN)	Stress amplitude (MPa)	Life(cycles)
50%	15.5	73.6	2319
40%	11.2	58.9	10,229
40%	11.5	58.9	8154
30%	9.7	44.2	26,225
30%	8.5	44.2	67,486
20%	5.6	29.5	734,741

tion produced an appreciable reduction in the fatigue strength of the material. At 10^6 cycles the fatigue strength is lowered from 25 MPa to about 14 MPa for 3000 hours of exposure suggesting that epoxy is more prone to oxygen salt water exposure (Figure 4.53).

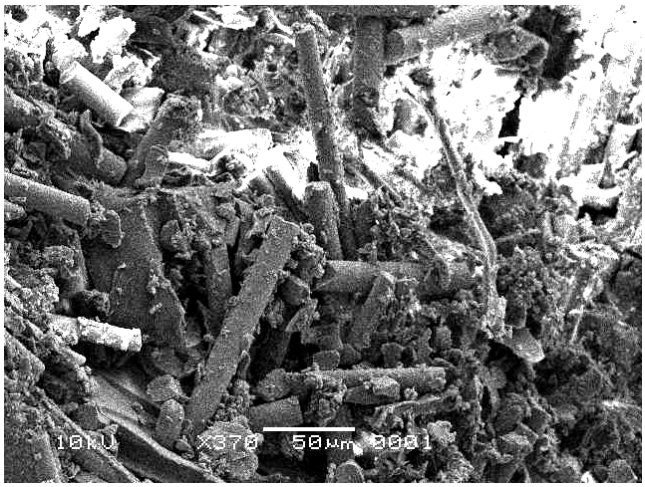

Figure 4.51: SEM microscopic image depicting fiber fracture and matrix fracture for the as received GFRE pipe material

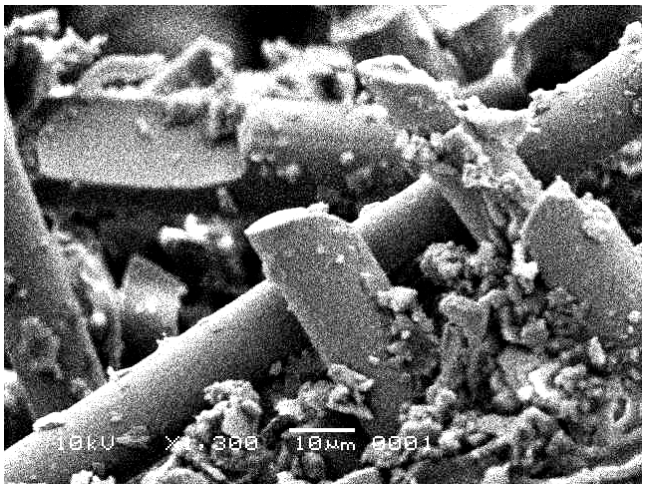

Figure 4.52: SEM microscopic image depicting fiber fracture and fiber denuded of matrix for the as received GFRE pipe material

Table 4.44: Epoxy Fatigue data for oxygen saltwater immersion for 1000 hrs

% of tensile strength	**P amp (KN)**	**Stress amplitude (MPa)**	**Life(cycles)**
50%	14.1	73.6	1869
40%	11.5	58.9	9426
40%	10.9	58.9	9603
30%	8.1	44.2	46,071
30%	8.9	44.2	35,986
20%	5.7	29.5	578,598

Table 4.45: Epoxy Fatigue data for oxygen-saltwater immersion for 3000 hrs

% of tensile strength	**P amp (KN)**	**Stress amplitude (MPa)**	**Life(cycles)**
50%	14.1	73.6	2084
40%	11.1	58.9	10,562
40%	12.1	58.9	5206
30%	8.7	44.7	46,770
30%	9	44.7	39,992
20%	5.6	29.5	545,628

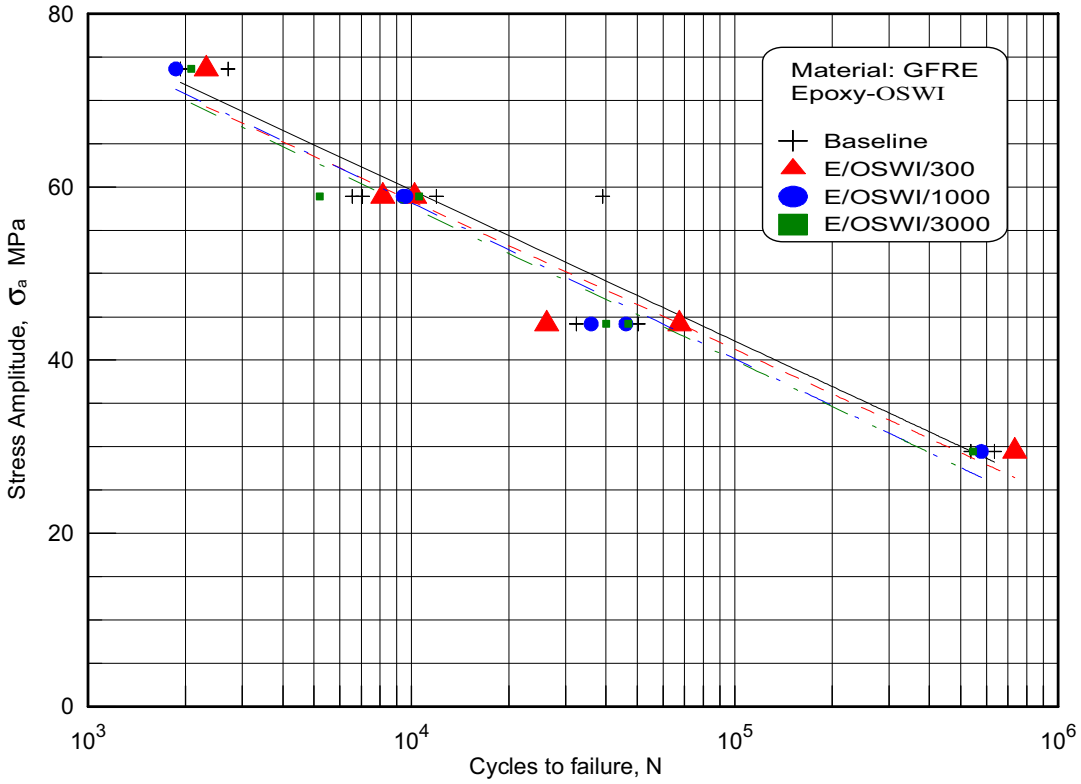

Figure 4.53: S-N curve for the GFRE pipe material exposed to OSWI immersion

4.3 Summary

In this chapter the experimental results of various environmental exposures are reported which includes both the outdoor and the accelerated conditions. Microscopic analysis was also done for the fatigue fractured specimens to study the surface morphology.

Chapter 5

Discussion

5.1 Tensile Results

5.1.1 Outdoor Exposures

Natural Exposure

Analysis of the tensile test results for the natural outdoor exposure reveal that 3-month natural outdoor exposure resulted in an improvement in the average tensile strength of GFRV1 by almost 7% from the base line value of 253 MPa. This improvement in the tensile strength and the stiffness modulus resulting from the 3 month outdoor exposure may be explained in term of

increase in the cross-linking of the molecular chains of the matrix resins due to curing of the vinyl ester resin during the first three month exposure.

Almost all of the curing seems to have occurred during the first three months. This was confirmed from the DSC tests. With increase in the exposure duration to 6 months, the GFRV1 pipes begin to experience the environmental damage. A slight lowering of the strength from its peak cured value of 271 MPa was observed after 6 and 12 months of outdoor exposure.

Most of curing seems to have been completed during the first three months. Following this period, weathering affects started its detrimental degradation on the material resulting in gradual decrease of strength with time.

Six months of exposure did not produce any noticeable change in the modulus value of GFRV1 composite (Table 4.1). However, the modulus value decreased by 47% as the exposure is increased to 12 months and also the strain to fracture (e_f) increased significantly suggesting that composite has become stiffer and more brittle. This may be possibly due to the plasticization of the matrix during the long term exposure. This plasticization had also caused degradation in the tensile strength of the material.

Crude Oil Exposure

In case of the oil filled pipes exposed to outdoor exposure conditions, tensile strength increased significantly with the exposure period. No significant variation in the modulus and the e_f values was noted (Figure 4.2). The average tensile strength of the GFRV1 pipe increased by about 13% for the 12 month crude oil exposure from the base line value of 253 MPa. This might be due to the oil ingression taking place at the fiber-matrix interface. This ingression might have assisted in improving the load transfer efficiency and thus resulting in increased tensile strength. A plausible statement can be made that the presence of oil for a period of 12 months might not have affected the strength and that the outdoor exposure alone has a positive effect on the strength due to curing. So one can assume that 12 month of oil exposure has not deteriorated these GFRV1 pipes.

Sea water immersion

In case of sea water immersion for a period of 12 months, a notable 6% increase in the average tensile strength was observed. However, the modulus decreased slightly by about 11% with an increase in e_f by 19% (Figure 4.3). This might be due to matrix plasticization and can be explained by the

diffusion of the water into the resin and resulting in resin softening. For immersion in sea water, water diffusion by the matrix is expected to be the main mechanism, however it is expected that this water absorption should reach a saturation level.

The above results indicate that the three natural weathering conditions have resulted in improving the tensile strength of GFRV1 (Figure 4.5). Longer exposure periods of GFRV1 pipes can lead to sound conclusions concerning these effects.

5.1.2 Accelerated Exposures

In this section, effect of various accelerated exposures on the environment are studied.

Dry heat

The specimens exposed to dry heat at 40^0C did not produce noticeable change in the tensile strength even after 10,000 hours of exposure. The strength remained close to base line value of 203 MPa (Figure 4.6). This suggests that dry heat exposure at 40^0C temperature was not high enough to cause any noticeable degradation of the material.

However, for the specimens exposed to dry heat condition at 70^0C, an improvement of about 8% in the tensile strength (from the base line value of 203 MPa) was observed consistently upto 10,000 hours of exposure. This improvement can be attributed to the curing process where the crosslink density increases causing an improvement in the tensile strength. The results suggests that during the first exposure periods of 300 and 1000 hours some plasticization of the may have also occurred due to thermal softening of the resin, causing increase in e_f. Later on with increase in the exposure period to 3000 hours, the an increase in modulus was noted. However, as the exposure time is increased beyond 3000 hours, this enhanced tensile strength (by 8%) remained stable up to 10,000 hours. This might be plausibly explained by a strong bond existing between the fiber-matrix interface (Figure 4.7).

The degradation of the material occurs more quickly at 70^0C in the exposure period than at 40^0C due to the weakening of chemical bond and interaction between fiber and matrix at higher temperature.

UV Exposure

The specimens exposed to UV radiation produced a significant decrease of about 10% (from 203 MPa to 183 MPa) in the tensile strength after 3000

hours of exposure (Table 4.7). This high degradation observed is due to absorption of energy which is strong enough to cleave covalent bonds and cause embrittlement of the resin. Hence, the composite starts becoming slightly stiffer only after 500 hours of exposure (Figure 4.8).

UV radiation is known to degrade the GFRP material; although only the outer layer tends to be affected. On prolonged exposure, the matrix might have hardened and a slight discoloration in the specimen was observed. Chemical reactions are induced when the functional groups absorb the UV radiation and free radicals are liberated which will trigger further reactions.

Humidity Exposure

In case of 100% humidity exposure, no significant effect on the tensile strength was observed up to 3000 hours of exposure. However, the modulus value varied significantly from 1.5 GPa to 2 GPa between 300 hours and 10,000 hours of exposure respectively (with base line value around 1.75 MPa). The initial decrease in the modulus value (with increase in e_f) can be attributed to the plasticization of the matrix which might indicate that moisture uptake was higher initially (300 hours) (Figure 4.9).

Later on with increase in exposure period for 10,000 hours, maximum

degradation was observed suggesting that longer exposure periods produce noticeable degradation in the material. The GFRV2 composite after its initial plasticization becomes slightly stiffer after longer exposure periods. These changes in the tensile properties are not merely associated with plasticization and hydrolysis of the resin through attack of ester link, but might have also been due to degradation at the fiber-matrix interface.

Similar to the 100% humidity exposure, composites exposed to ambient humidity condition did not produce any significant change in the tensile properties until 3000 hours of exposure. A 12% decrease was noted in tensile strength after 10,000 hours of exposure suggesting that longer exposure period produce noticeable degradation (Figure 4.10).

Salt Spray Exposure

The specimens exposed to salt spray condition did not produce any noticeable change initially, however exposure beyond 3000 hours resulted in about 15% decrease in the tensile strength for 10,000 hours. The modulus varied significantly from 1.52 GPa (for 300 hours) to 1.82 GPa (for 10,000 hours) from the base line value of 1.75 GPa (Figure 4.11). Initially for 300 hours, it is the matrix plasticization which causes the vinyl ester resin to soften and

swell and hence resulted in stiffness reduction by about 13%. This can be explained by the disentanglement of molecular chains which takes place at ease as the moisture acts as lubricant and hence resulting in resin plasticization.

Later on with increase in exposure time for 10,000 hours, moisture ingress to the fiber-matrix interface increases and might leach out the binding agent and hence resulting in maximum reduction of 15% in the tensile strength. Also, the GFRV2 composite after its initial plasticization becomes slightly stiffer at longer exposure period which was similar to the one noted for humidity condition.

Oxygenated salt water immersion Exposure (OSWI)

The specimens exposed to the OSWI condition resulted in notable degradation in the tensile strength with exposure time. Probably, the immersion in water might have prevented curing of the GFRV2 composite and hence resulted in 9% reduction in strength after 1000 hours and also the modulus value increased by 50% making the composite stiffer. As the exposure period reached 6000 hours, a significant reduction of 19% in tensile strength and 11% in the modulus value was observed, suggesting that OSWI exposure (at longer exposure periods) resulted in plasticization of the matrix (Figure 4.12).

This maximum degradation in tensile strength after 6000 hours of exposure could be due to the leaching out of the un reacted (uncured) chemicals from the resin matrix leaving the fibers with no protection and making them more devoid of resin (i.e reducing the interfacial adhesion between fiber and the matrix). Also, the vinyl ester resin which possess few hydrolyzable groups pick less amount of water and thus causing maximum reduction in tensile strength.

5.1.3 GFRE composite

In case of GFRE composites, the samples exposed to the Oxygen -salt water immersion observed a noticeable change in the tensile strength with 10% reduction after 3000 hours of exposure (Figure 4.14). This reduction in the mechanical properties is due to the degradation of the resin (during hydrolysis reactions) where the ester bonds are destroyed. Hence, less bonding occurs between these chains which can slide past each other at greater ease. Also the water uptake by the GFRE composite either by resin (diffusional) or through fiber-matrix interface (through capillary action which is more predominant) might have reduced the tensile strength more predominantly.

A slight degradation by 7% in the modulus after 1000 hours of exposure

was later regained with increase in the exposure time of 3000 hours suggesting that the moisture absorption has reached its saturation and the GFRE composite is trying to achieve its base line modulus (Table 4.8).

5.2 Fatigue Results

5.2.1 Outdoor Exposures

Natural Exposure

The fatigue test results for the GFRV1 material exposed to natural outdoor environment in Dhahran region for a period of 12 months was shown Figure 4.16. Results indicate an enhancement of the fatigue life by a factor of about 2.5 after 3 months of exposure. This improvement in fatigue resistance may have occurred due to crosslinking of the polymer chains which may have resulted due to the curing of the matrix. This curing of the vinyl ester resin can be from the combined effects of UV radiation and temperature components of the outdoor exposure during the first three month outdoor exposure. This crosslinking is expected to improve the interfacial fiber matrix binding and promote an efficient matrix to fiber load transfer, which should enhance the material fatigue resistance.

The improvement observed in the fatigue resistance of the GFRV1 material after 3 months slightly begin to diminish after 6 months. However, the fatigue strength still remained higher than the fatigue strength of the as received (un-exposed) material. These results suggest that the environmental conditions begin to induce their detrimental effects on the material after the initial beneficial effect attributed to curing during the initial 3 months exposure. The SEM analysis of the fractured surfaces for the 12 month outdoor exposures reveal a clear degradation in the material. There was a clear indication of matrix embrittlement which resulted in matrix cracks (Figure 4.19) and also the fiber fracture surfaces are clearly visible. The brittle fracture of the fiber can also be clearly seen for 12 month exposure as shown in Figure 4.18.

Crude Oil Exposure

The fatigue results of GFRV1 pipe material exposed to the crude oil results in an improvement in the fatigue resistance and fatigue life with increase in exposure time. A fatigue life enhancement by a factor of 2.5 was noted for 12 month exposure. This improvement was more predominant in low cycle regions (Figure 4.20). Oil ingress at the fiber-matrix interface might

have helped in improving the load transfer efficiency and hence resulted in improvement in the fatigue strength.

Sea Water Immersion

The fatigue results for the 12 month immersion in the gulf sea water did not show any degradation of the fatigue strength as seen in Figure 4.21. It is generally assumed that water penetrates GFRP composites more readily at the resin-glass interface than by diffusion through the matrix. It should be noted that 365 days of sea water immersion is relatively short in comparison to the service life expected of GFRP and the presence of water might affect the properties of the composite after long immersion periods.

5.2.2 Accelerated Exposures

Dry heat Exposure

In case of Dry heat exposure at 40^0C, no noticeable effect was observed upto 3000 hours of exposure. However, a slight reduction in the fatigue life by a factor of 4 was observed for longer exposure period of 10,000 hours (Figure 4.26). It is safe to assume at this stage that this temperature was not high enough to degrade the GFRV2 composite.

The effect of dry heat condition at a higher temperature of 70^0C results in a drastic improvement in the fatigue strength for the GFRV2 material. In general, the as received GFRV2 shows poor fiber-matrix debonding of the matrix (Figure 4.22). This situation was however improved during the dry heat at 70^0C exposure. An improvement in the fatigue resistance was observed due to crosslinking phenomenon during the curing process and also due to more restricted chain entanglement and chain sliding.

The microscopic images for 1000 hours of dry heat (at 70^0C) show brittle cleavages of the matrix which might be due to resin embrittlement caused by exposure to high temperature and resulted in a stiffer matrix (Figure 4.29). Reduction in the fatigue strength was also observed for this exposure period. This might be due to poor adhesion between the fiber and the matrix, during which the matrix behaves in a rather brittle manner without much matrix plasticization and even the matrix cracks which are initiated at the fiber-matrix interface are also clearly visible (C) as shown in (Figure 4.30).

During fracture, the matrix which has been the supporting the fibers assisted in the improvement of fatigue strength (almost 3 MPa increase at 10^4 failure cycles)(Figure 4.27)

However, as the exposure period further increased to 3000 hours, an im-

provement in the adhesion between the fiber and matrix was clearly noticed (Figure 4.31) and this adhesion improvement can be due to the plasticization of the matrix (Figure 4.32). There are certain matrix cracks visible which might have initiated from the fiber/matrix interface (Figure 4.33). For dry heated specimens, shear fracture of the fibers was also seen suggesting that fibers which are generally protected from the environment by the matrix are also severely affected by heat as indicated in Figure 4.34. Fracture surface also confirms the existence of matrix debris bonded to their fiber surface.

Even 10,000 hours of dry heat exposure did not seem to degrade the GFRV2 material; rather resulted in an increase in the fatigue strength by 5 MPa and fatigue life by 7 orders at low cycle regions.

UV Exposure

The fatigue test results for the specimens exposed UV radiation shows a degradation in fatigue strength by 6 MPa and fatigue life by 3 orders for 500 hours of exposure. This high degradation might be due to the absorption of radiation energy which was strong enough to cleave the covalent bonds and cause embrittlement of the vinyl ester resin. A low exposure period of 500 hours also resulted in such a noticeable degradation in the fatigue

test results. This explains the significance of UV Exposure on the GFRV2 composites. The UV radiation exposure appears to be the most detrimental among all the accelerated environmental conditions thus far studied.

Humidity Exposure

The GFRV2 composite exposed to both 100% humidity condition and the ambient humidity condition did not produce any clear trend of either enhancement or degradation in the fatigue properties even after 10,000 hours. Longer exposure period to humidity conditions did not alter the fatigue properties and hence the durability of the composite was not affected.

Salt water Spray

For the GFRV2 composites exposed to the salt spray at room temperature a slight decrease in the fatigue life (by 2 orders) and fatigue resistance (by 3MPa) were observed for low exposure periods. This reduction in the fatigue properties can be mainly attributed to the plasticization process where the moisture was absorbed by the matrix and hence causing the matrix to swell. At higher exposure periods of 10,000 hours, this degradation effect was less pronounced (Figure 4.38).

Fractographic images for 3000 hours show the degradation of matrix surface by salt spray which might be due to matrix swelling and cavitation and this has weakened the matrix and hence plasticization was not visible for this exposure (Figure 4.41. Matrix shattering and brittle failure of the matrix was clearly visible with numerous tearing also seen with evidence of matrix debris. Fiber surfaces are generally clean (i.e fibers are devoid of resin) suggesting the lowering of adhesion between the fiber and the matrix for this 3000 hours exposure (Figure 4.42. This suggest that the medium has significantly affected the coupling agent which are applied to the glass fibers to improve bonding and to increase water resistance. Significant matrix degradation was seen by the salt spray as seen in (Figure 4.40.

Oxygenated Salt water Immersion (OSWI)

The GFRV2 specimens exposed to OSWI observed a notable degradation in the fatigue strength (by 4 MPa) and fatigue life (by 2.5 orders) for 3000 hours of exposure (Figure 4.43). This reduction may be attributed to the composite debonding caused by the diffusion of water into layers and interfaces between fibers and the resin. Long term water action could cause solution of some fiber resin components and would lead to debonding of the fiber resin system.

The effects of oxygen-salt water on the fatigue behavior of the composite have been explained as GFRV2 can absorb water and have a influence on the fibre-matrix interface and well on the matrix properties. The behavior of any composite depends on the efficiency of the fiber-matrix interface and this can be reduced by the presence of water. These fractured seems to be driven by the water induced failure of the fiber/matrix interface, which led to an acceleration of damage of the composite.

Matrix cracking can be seen to have existed (Figure 4.45) for 300 hours of exposure; but its effect seems to absent for 3000 hours of exposure suggesting the fiber debonding was more predominant for higher exposures (Figure 4.50). During fatigue loading, the micro cracks were observed to be followed by debonding between the fibers and matrix similar to the one observed by Dharan [65]. The cohesion at the fiber/ matrix interface was reduced for 300 hours due to weakening of bond by the presence of moisture (Figure 4.47), increasing the incidence of fiber pullout at the fracture surface. Matrix fragmentation (Figure 4.46) was also witnessed for 300 hours of exposure.

There is an evidence of salt debris (The deposits seem to be NaCl crystals) on the fracture surface for 3000 hours of exposure (Figure 4.48) which was less evident for 300 hours of exposure. There was also evidence of delam-

ination and fiber splitting of the fiber bundle because of the dissolution of the amorphous matrix for 3000 hours of exposure (Figure 4.50). Clear flat fiber fracture (like brittle solid) was seen for 3000 hours of exposure (Figure 4.49) which might be due to the embrittlement of glass fiber (due to oxidation) that was less predominant for 300 hours of exposure. Rough surfaces of the glass fibers indicated that the water had attacked the glass.

The primary effect of water entering at the fiber-resin interface is to chemically interact with the interface and the coupling agent and to form an Si-O-Si bond at the glass surface; water could cause bond scission. This could result in complete debonding between the matrix and fibers with consequent adverse effects of decreased stress transfer efficiency. Degradation at the interface can been ascribed to primary bond scission, weakening of secondary bonds or lubricity effects. Regardless of mechanism, degradation is expected to occur at the glass resin interface under the influence of water.

5.2.3 GFRE Composite

The exposure of GFRE composites to 100% oxygenated salt water immersion produced a slight reduction in the fatigue strength of the material. Similar observation was also noted for the GFRV2 material when exposed to OSWI

condition. This might be due to hydrolysis of the epoxy resin, and when this resin was hydrolyzed, the ester bonds are destroyed and with less bonding between these chains, they slide past each other at greater ease. This resulted in the lower values of the fatigue properties. A further reduction in the fatigue properties after 3000 hours of exposure was not noted. This might suggest that the moisture absorption has reached its saturation after 1000 hours of exposure (Figure 4.53).

5.3 Summary

In this chapter, the experimental results which were mentioned in the previous chapter were discussed and the efforts were made to correlate each exposure condition with different mechanisms.

Chapter 6

CONCLUSION

This work mainly focussed on evaluating the effect of various natural and accelerated environmental conditions on the tensile and the fatigue properties of the vinyl ester and epoxy based glass fiber reinforced thermoset pipes. It must be pointed out that duration of this thesis was not long enough to study all the environmental effects to their desired extent. However, this study yielded some results based on which generalized conclusions can be drawn which are presented as follows:

1. Analysis of the results for the natural outdoor exposure conditions reveal that the exposure for the duration of 3 months has resulted in an increase in both the tensile and fatigue strengths of GFRV1 composite

pipes. This improvement is related to the cross linking of the matrix chains during a post curing process.

2. During the next 9 months of exposure, the GFRV1 experienced a degradation in its tensile strength. A possible explanation for this degradation is that the material reached its full post curing within the first three months, after which environmental degradation started to take effect.

3. For the pipes filled with crude oil and exposed to natural outdoor conditions, as well as for pipes immersed in gulf sea water, an improvement in the tensile strength and fatigue strength was observed.

4. For specimens exposed to dry heat condition at 70^0C, an increase in the tensile strength was observed. This improvement in strength could once again be related to matrix chain crosslinking, due to curing. No noticeable change in the tensile strength was observed for exposure at 40^0C.

5. For UV exposures, a significant degradation in both the tensile and the fatigue resistance was noticed.

6. The GFRV2 specimens exposed to both salt spray and humidity condi-

tions did not show any noticeable degradation even after 10,000 hours of exposure. This suggests that the composite durability is unaffected by these two conditions.

7. For oxygen salt water immersion, the damage process seems to be driven by the water induced failure at the fiber/matrix interface, which led to an acceleration of damage of the composite. The cohesion at the fiber/matrix interface is reduced by the presence of moisture. The fiber surface was smooth and wide voids were seen between fibers and matrix. The failure was dominated by the fiber/matrix interface debonding.

8. Among all the moisture based accelerated exposures, the oxygen salt water immersion seems to cause the highest degrading effect on the composite.

9. For GFRE Composites, exposure to oxygen salt water immersion resulted in higher degradation in the material strength compared to GFRV2 composites.

6.1 Future work

1. The work should continue to include extended exposure periods upto 60 months to generate additional data on the tensile and fatigue resistance of the GFRV and GFRE thermoset pipes.

2. A model should be developed to correlate the results of the accelerated exposure condition to the natural outdoor conditions.

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